

Chapter 2

Optical-Beam-Induced-Current Imaging of Planar Polymer Light-Emitting Electrochemical Cells

Faleh AlTal and Jun Gao

Abstract In this chapter, we describe optical-beam-induced-current (OBIC) and scanning photoluminescence (PL) imaging of extremely large planar LECs that have been frozen to preserve the doping profile. This complements the basics described in Chap. 1 with respect to device mechanism and characterization. We succeeded in resolving the depletion width, for the first time, of a frozen LEC *p-n* junction and a frozen LEC *p-i-n* junction. These optical scanning results reveal a surprisingly strong built-in potential that is independent of the electrode work function and an extremely narrow junction depletion region that is about 0.2% of the interelectrode spacing. These findings provide new insight into the electronic structure of the LEC junction. Since only about 0.2% of the entire device area is photoactive in response to an incident optical beam, the effective junction width (or volume) of polymer-based LECs must be dramatically increased to realize a more efficient device.

Keywords *P-i-n* junction • *P-n* junction • Electrochemical doping • Optical-beam-induced current • Light-emitting electrochemical cell

2.1 Polymer Light-Emitting Electrochemical Cells

2.1.1 Background

A light-emitting electrochemical cell (LEC) is a solid-state, two-terminal device that employs a mixed ionic/electronic conductor as the active layer—see Chap. 1 for more details [1–7]. The first LECs were demonstrated by Pei et al. and consisted of a luminescent conjugated polymer as the emitter, and a polymer electrolyte as the ion conductor sandwiched between two electrodes [8]. A direct current (DC) bias,

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comparable to the luminescent polymer energy gap, is required to activate a polymer LEC. Charge injection at the positive electrode (anode) and the negative electrode (cathode) leads to the oxidation and reduction of the luminescent polymer. Meanwhile, the mobile ions from the polymer electrolyte redistribute and compensate the injected electronic charges, causing in situ electrochemical doping of the luminescent polymer. The doped polymer is electrically neutral but has elevated electronic conductivity due to the extra, injected electronic charges. With remarkable insight, it was hypothesized by the inventors of LECs that the in situ doping was a dynamic process: doping initially occurred at the electrode-polymer interfaces, but the doped regions would expand until they meet to form a p - n junction. The formation of the p - n junction opens up a continuous pathway for the electronic charges, namely electrons and holes, which recombine in the junction region to give off light emission [9]. The LEC operation mechanism, as described above, is depicted schematically in Fig. 2.1. Light emission in an LEC is the result of radiative recombination of the injected electrons and holes in the vicinity of the junction. In this regard, the polymer LEC is analogous to a conventional p - n junction light-emitting diode (LED) in that both contain a semiconductor homojunction. A polymer LEC is therefore fundamentally different from a polymer LED made with the same luminescent polymer [10].

The polymer-based LEC was developed to address two main drawbacks of conventional polymer LEDs. The active layer of a prototypical polymer LED is a pristine light-emitting polymer film. For visible light-emitting applications, the energy gap of the polymer needs to be between 1.6 and 3.1 eV. Due to the large energy gap, undoped polymer films have high resistivity and need to be very thin in order to inject a sufficient amount of current. The ultrathin (ca. 100 nm) polymer film, however, is prone to pinholes and the effect of exciton quenching [11]. Moreover, the injection of electrons and holes needs to be balanced for maximum electroluminescence (EL) efficiency. To facilitate electrons injection, a low work function reactive metal cathode is commonly used. The highly reactive cathode material (such as calcium) increases the chance of device failure unless the polymer LED is carefully encapsulated. The polymer LEC, by contrast, operates on in situ electrochemical doping of the luminescent polymer due to the presence of mobile ions in the composite material. The doped polymer is much more conductive than a pristine one so that a thicker active layer could be used. The high conductivity of the doped LEC film also ensures strong and balanced charge injection at the electrode interfaces. Regardless of the electrode work function, efficient charge

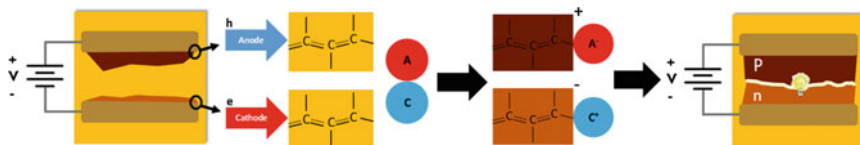


Fig. 2.1 Illustration of doping propagation and junction formation process in polymer-based LECs. h stands for holes, e stands for electrons, A stands for anions and C stands for cations

injection can occur via quantum mechanical tunnelling between a metal electrode and a heavily doped semiconductor. Heavy doping is in fact how an ohmic contact is made in conventional inorganic semiconductor devices. Indeed, highly efficient sandwich LECs had been demonstrated very early on with air-stable cathode materials and without express optimization of the active layer thickness [12–14].

The unique advantages of LECs have led to a renaissance of interest in these devices in recent years [2, 15–23]. LECs can be made with not only luminescent polymers and polymer electrolytes, but also ionic metal complexes or low-cost small molecules [24–32]. The LEC operation mechanism is inherently complex due to the presence of both ionic and electronic charges in a mixed ionic/electronic conductor. The fundamental operating mechanism of polymer-based LECs, for example, had been a subject of intense debate [33, 34]. The aim of many studies, both theoretical and experimental, had been to elucidate the basic processes of LECs and the properties of the LEC junctions [35–40]. For polymer-based LECs, it is established that in situ electrochemical doping and junction formation are the fundamental processes that dictate the dynamic activation/turn-on behaviour of LECs, as well as the static junction properties. However, we still lack knowledge about the basic properties of an LEC p - n or p - i - n junction. In this chapter, we describe our recent experimental work on the scanning optical imaging of frozen planar LECs to probe the electronic structures of an LEC junction. This is meant to complement the basics described in Chap. 1 with respect to device mechanism and characterization. In brief, we performed four consecutive optical-beam-induced-current (OBIC) and scanning photoluminescence (PL) imaging of LECs with a planar (versus sandwich) configuration. We devised four different scanning setups, each with an increasing scanning resolution than the previous one [41–44]. We succeeded in resolving the depletion width, for the first time, of a frozen polymer p - n junction and a polymer p - i - n junction. These optical scanning results reveal a surprisingly strong built-in potential that is independent of the electrode work functions and an extremely narrow junction depletion region that is less than 0.2% of the interelectrode spacing. These findings have profound implications on the development of more practical and efficient LECs, as well as the fundamental science of mixed conductors—e.g. see Chaps. 4, 5, 6, and 10. The scanning measurements were performed on extremely large, frozen-junction planar LECs. Gao and his colleagues were the inventors of both extremely large planar LECs and frozen-junction LECs, two key LEC concepts that will be briefly introduced below before the optical scanning experiments are presented in Sects. 2.2, 2.3, and 2.4.

2.1.2 Frozen-Junction LECs

Despite possessing some very attractive device characteristics, polymer LECs are not without drawbacks. The very operation mechanism responsible for LEC's insensitivity to the active layer thickness and the electrode work function also

brings serious comprises. The turn-on or activation of an LEC typically takes seconds or even minutes as the junction is slowly established by the slow moving ions [12, 14, 45]. Unlike the doping of silicon by chemical diffusion, the in situ electrochemical doping of an LEC 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 LEC junction will eventually disappear as the doped regions relax back to the undoped state. Therefore, LECs are slow to turn-on and exhibit strong hysteresis if they are turned on before reaching a fully relaxed state from a previous operation [46]. LECs 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 LECs are not suitable for high intensity applications.

It is apparent that a fixed LEC junction is desirable, since it will retain all the advantages of LECs, while also be fast and stable. In an LEC, fixing the junction means fixing the counter ion placement. Realizing that the ion transport/mobility in a polymer electrolyte is strongly temperature dependent, Gao et al. devised a simple method to fix the LEC junction by cooling the cell after the junction formation [46, 47]. When the LEC temperature is below the glass transition temperature (T_g) of the polymer electrolyte, the ions, and therefore the LEC junction, are immobilized. The first demonstration of a frozen LEC 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 an Indium-Tin-oxide (ITO) electrode and an aluminium electrode. 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 reached the target temperature. Second, the target temperature of 100 K was well below the T_g of PEO (about 208 K). This ensured that the LEC junction was fully stabilized. The resulting "frozen-junction" LEC exhibit much faster response time (μ s) than the same cell operated at room temperature. In a frozen-junction LEC, the ions are immobilized and the device response time is no longer limited by the slow doping process. The frozen-junction LECs also exhibit diode-like current versus voltage versus light intensity (I - V - L) characteristics, as shown in Fig. 2.2. Significant current and EL had only been observed under forward bias, here defined 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 LECs, which can conduct and emit under both forward and reverse bias at the same time, or the polymer LEDs, whose polarity is fixed.

The frozen junction also brings a new functionality to the LEC. For the first time, an activated LEC can operate as a photovoltaic (PV) cell for power generation. Figure 2.3 shows the I - V traces of a frozen-junction cell in dark and under

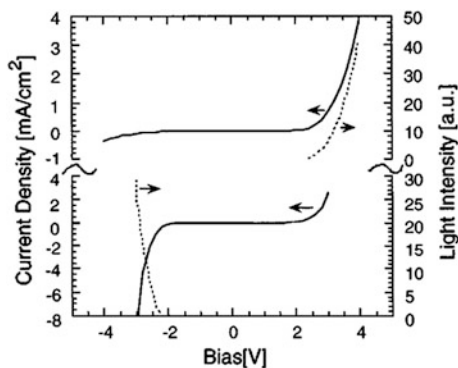
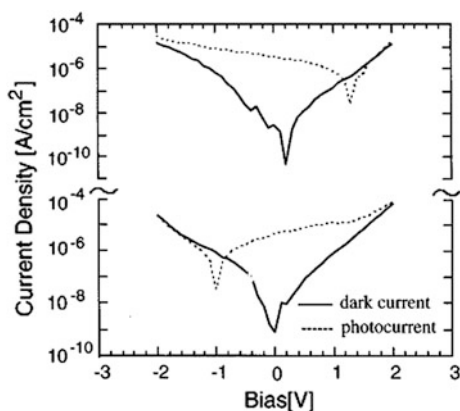


Fig. 2.2 Current and light vs voltage (I - V - L) data measured at 100 K (upper curves) after cooling under +4 V bias. The LEC was subsequently heated to 300 K without external bias, then biased at -3 V and cooled (after reaching steady state) to 100 K. The I - V - L characteristics (lower curves) were reversed after prebiasing at -3 V, with roughly mirror symmetry relative to 0 V. Reprinted with permission from reference [47]. Copyright (1997) American Institute of Physics

Fig. 2.3 The photovoltaic response of a frozen sandwich LEC 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. Reprinted with permission from reference [47]. Copyright (1997) American Institute of Physics



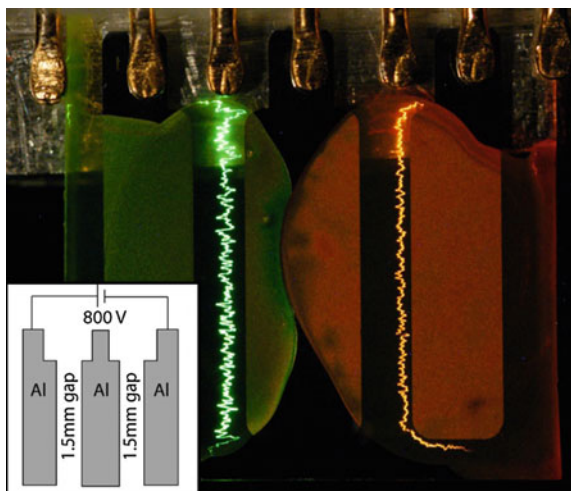
illumination. The low rectification ratio of the dark I - V curves can be attributed to the high resistance of the film at low temperature. The cell, however, showed a pronounced photovoltaic response in either polarity, as shown by the dashed curves. It is remarkable that the same cell can exhibit either 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 photovoltaic response of a frozen-junction LEC, just like its EL, is no longer dependent on the electrode work functions. Rather, the LEC 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 LEC junction. Adding an electron-accepting polymer to the LEC blend created a more efficient frozen-junction polymer photovoltaic cell [48].

While it is fairly straightforward to cool an activated LEC to stabilize its junction in a laboratory, eventual application of frozen-junction LECs requires the junctions, once formed, to be frozen at room temperature. Progress toward this goal has been made by using electrolytes with a high T_g [49, 50]. The junction is formed at elevated temperatures and the cell is subsequently cooled to room temperature. The LEC junctions can also be fixed chemically [51–56]. One method used ion pair monomers in the LEC blend [51]. Upon activation, these ions dope the polymer and cause radical-induced polymerization that would significantly reduce the ions mobility and fix the junction. Pei et al. used PEO oligomer capped with methacrylate as the ions conducting component. It was found that polymerizing the methacrylate group during junction formation results in a stable junction with lifetime and efficiency comparable to polymer LEDs [57]. Another approach utilized ionic trapping polymers to establish a permanent junction after junction formation [54]. Also, fixed junctions were formed by incorporating cross-linkable materials that were cured after the junction formation [58, 59]. Finally, our group recently showed that when the ion solving/transporting material such as PEO was removed altogether, the resulting cell, now only contains a luminescent polymer and a lithium salt, could still be activated by applying a much higher bias voltage. The activated cells exhibit characteristics of LECs with strong evidence of doping. More important, the activated state was stable for more than 100 hours without an applied bias. This is the longest reported shelf-life of a frozen junction at room temperature [60, 61].

2.1.3 *Extremely Large Planar LECs*

Unlike organic or polymer LEDs, LECs can operate in both sandwich and planar configurations. In a planar configuration device, the overall device resistance is dominated by the bulk resistance of the active layer, which can be enormous for an undoped semiconducting material if the interelectrode spacing is large. For example, a planar polymer LED with an interelectrode spacing of 30 μm exhibited an EL turn-on voltage of 500 V and was only operational at liquid nitrogen temperatures [62]. A planar LEC of similar dimensions, however, can be turned on to emitted light with a mere 4 V bias [8]. In an LEC, the presence of mobile ions and the subsequent in situ electrochemical doping render the active film highly conductive. The images of these planar LECs offered the first visualization of an LEC junction [8, 9, 63]. The relatively small size (interelectrode gap size) of these early planar LECs means that they were difficult to fabricate and to study. There had been almost no follow-up studies of planar LECs in the late 90s and early 2000s. In 2003, Gao and Dane demonstrated planar LECs 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 Fig. 2.4. The millimetre-sized, extremely large planar LECs are easy to fabricate via shadow masking compared to photolithographic patterning. More important, the slow turn-on process of these planar LECs

Fig. 2.4 The photograph of two working 1.5 mm polymer-based LECs in series under 800 V bias. Also shown is the device configuration and biasing condition. The green-emitting device is made with a green emitter; and the orange-emitting device is made with MEH-PPV. The shutter speed is 5 s and the aperture is f/10. Reprinted with permission from reference [64]. Copyright (2003) American Institute of Physics



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 LEC film affects not only its electrical conductivity but also its optical properties. Doping introduces mid-gap impurity states that quench the PL of the luminescent polymer [65, 66]. The optical effect of doping had been exploited by Gao and Dane to elucidate the very doping process of LECs [67]. Extremely large planar LECs were imaged under UV light illumination, and for the first time, the dynamic LEC doping process had been visualized. Figure 2.5 displays the time-lapse PL images of a 1.5 mm planar LEC under a voltage bias of 140 V. The LEC film exhibits the characteristic orange-red PL of MEH-PPV. Also visible are finger-like, darkened regions expanding from the anode toward the cathode. On the cathode side, faint but discernible darkening of the polymer film could be observed. These darkened regions are, in fact, *p*- and *n*-doped regions whose PL had been partially quenched. The darker *p*-doped region expanded at a faster speed than the *n*-doped region. The expansion stopped once the propagating doping fronts had met to form a *p-n* junction. Moreover, strong EL could be observed in the last image from the forward-biased *p-n* junction. These visualizations provide indisputable proof that doping did occur in a polymer LEC, and the formation of a *p-n* junction was necessary for EL to occur.

From the time-lapse images of planar LECs, the average doping propagation speed was extracted and shown to be highly sensitive to the operating temperature [68]. By moderately increasing the operating temperature, Gao et al. successfully demonstrated the largest planar LEC ever with a gap size of over 10 mm [69]. Edman et al., on the other hand, showed that planar LECs with a gap size of 1 mm could be turned on with only a 5 V bias when heated to 360 K [70]. Figure 2.6 shows an example of the largest planar LEC under UV illumination during the activation process [71]. In this cell, both *p*- and *n*-doping are clearly visible. Also,

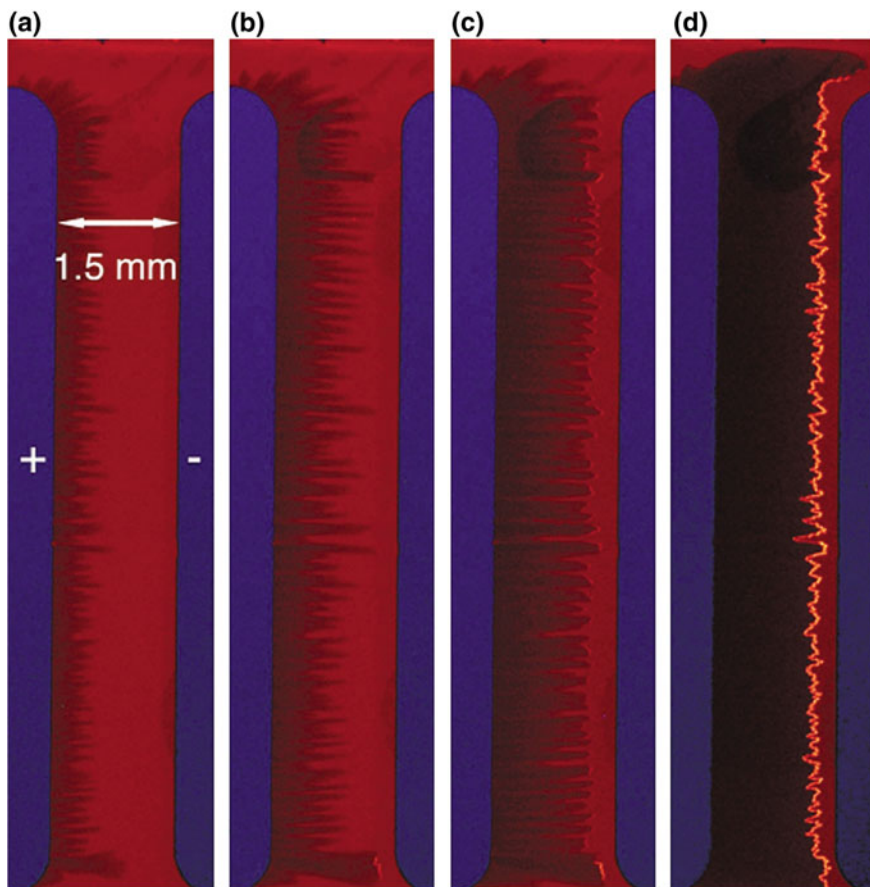


Fig. 2.5 Photographs of a working 1.5 mm MEH-PPV polymer-based LEC under 365 nm UV illumination. The device was tested at 310 K under a voltage bias of 140 V. The electrode to the left is positively biased (anode, denoted as “+”) relative to the electrode to the right (cathode, denoted as “-”). The photographs were taken at different times after the application of the voltage bias. **a** 8 min; **b** 13 min; **c** 18 min; **d** 43 min. The exposure time is 20 s. The aperture is $f/10$. Reprinted with permission from reference [67]. Copyright (2004) American Institute of Physics

once again EL was only observed when the p - and n -doping fronts had made contact to form a p - n junction. 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 the cell surface in a micromanipulated cryogenic probe station.

The time-lapse fluorescence imaging of extremely large planar LECs has proven to be a powerful and versatile technique in the elucidation of LEC processes. The effect of thermal annealing, [72] electrode work function, [73, 74] electrolyte salt, [75–77] and operating voltage [78] had all been studied. The static doping profile of

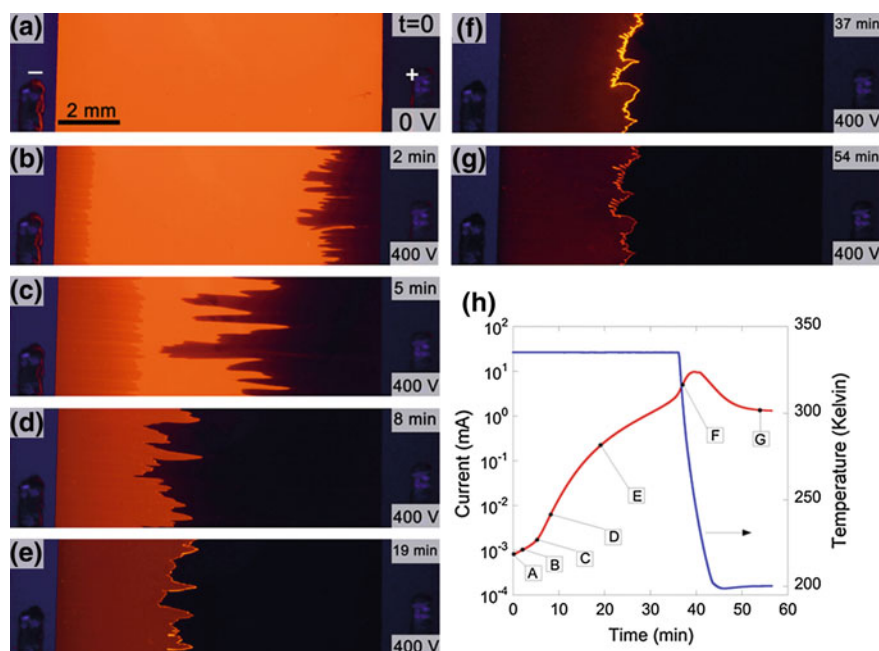


Fig. 2.6 Time-lapse fluorescence imaging of a 10.4 mm MEH-PPV: PEO: CsClO₄ planar LEC during turn-on and cooling. A fixed DC bias of 400 V was applied to turn on the cell, which was at 335 K and under UV illumination. Time since the DC bias was applied to the cell: **a** no bias **b** 2 min **c** 5 min **d** 8 min **e** 19 min **f** 37 min **g** 54 min. Panel H shows the cell current and temperature as a function of time after the DC bias was applied. Uniform enhancement (Level adjustment in Photoshop) has been applied to images A-G. Reprinted with permission from reference [71]. Copyright (2011) American Chemical Society

a frozen-junction LEC had been directly observed in a frozen planar LEC [68]. Heating the frozen cell briefly, however, led to partial relaxation of doping and the formation of a *p-i-n* junction [79]. 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 [80].

2.2 Scanning Optical Imaging of Planar LECs

2.2.1 The Optical-Beam-Induced Current (OBIC) Technique

Passive, time-lapse fluorescence imaging of the entire planar LECs has led to many discoveries described above. The fully exposed surface of a planar LEC also offers

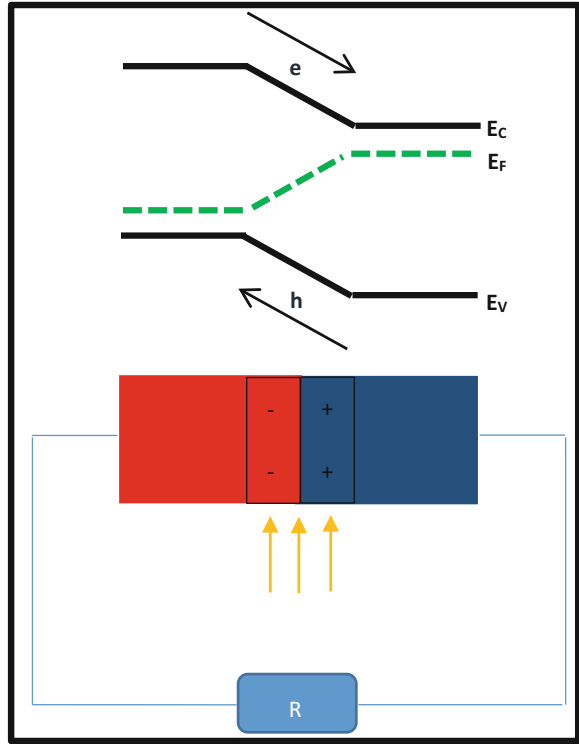
a unique platform to perform spatially resolved, electrical probing of local electrical properties of the cell. Recently, scanning probe microscopic techniques have been applied to planar LECs to determine the electric potential distribution across biased planar LECs operated at room temperature [81–84]. With the extremely large 10.4 mm planar cell shown in Fig. 2.6, Gao and Hu used a micromanipulated cryogenic probe station to map both the electrical potential and the conductivity profiles of the frozen cell [71]. These studies establish that the planar LEC is doped, and a p - n junction is formed. The p -doped polymer (MEH-PPV) is much more conductive than the n -doped polymer, and the level of doping is not constant in each of the doped regions.

While the above scanning probe studies aim to map the spatial distribution of an externally applied potential, the LEC junction also possesses a built-in potential/field just like a conventional p - n junction. The presence of the junction built-in potential/field is evidenced by the strong PV response of a sandwich frozen-junction LEC described in Sect. 2.1.2. In planar frozen-junction cells, V_{OC} approaching the magnitude of the band gap energy has been observed despite the use of identical electrodes [80].

For any semiconductor homojunction, it is important to know the junction depletion width in order to design a more efficient device structure. The depletion width plays a major role in determining the response time, carrier recombination and photogeneration of the device. The optical-beam-induced current (OBIC) technique is especially well suited to probe the electronic structure of a semiconductor junction [85–89]. In OBIC measurement, a focused light beam is scanned across the device; a photocurrent is generated when the focused beam illuminates the depletion region. In neutral p - or n -doped regions, by contrast, a null OBIC signal is expected due to the absence of a built-in field that can sweep the photo-generated charge carriers before they recombine. Figure 2.7 illustrates a p - n junction under illumination when connected to a load resistor. Absorption of photons with energy larger than the band gap energy generates electron and hole pairs. The electrons and holes generated in the depletion region are subsequently swept to opposite directions shown. This creates a photocurrent and a voltage drop across the junction. The flow of a net current is reflected by the gradient in the Fermi level of the junction. It should be mentioned that the OBIC technique is typically carried out under the short-circuit condition where the detected OBIC is a short-circuit current. In addition, photogeneration just outside of the depletion region (within one diffusion length) can also give rise to an OBIC signal when the photogenerated charge carriers enter the depletion region by diffusion.

In the absence of an externally applied electric field, the drift-diffusion equations that govern the current generation in a semiconductor are given by

Fig. 2.7 A schematic of a p - n junction under light illumination and the associated energy band diagram



$$\begin{aligned}
 J_n/q &= \frac{k_B T}{q} \mu_n \nabla n - \mu_n n \nabla u \\
 J_p/q &= -\frac{k_B T}{q} \mu_p \nabla p - \mu_p p \nabla u \\
 \Rightarrow J_T/q &= \frac{k_B T}{q} (\mu_n \nabla n - \mu_p \nabla p) - \nabla u (\mu_n n + \mu_p p),
 \end{aligned} \tag{2.1}$$

where J is the current density, q is the elementary charge, k_B is the Boltzmann constant, T is the temperature, n is the free electrons concentration, p is the holes concentration, μ is the mobility coefficient and u is the electrostatic potential. The subscripts n , p and T stand for electrons, holes and total respectively. The first part of the last line in the equation is the diffusion part of the current density, while the second part is the drift part. The Einstein relation was assumed to be valid. The electron and hole components of the diffusion current counter each other and vanish when the diffusion coefficients of electrons and holes are equal, assuming balanced electron-hole generation/recombination. Also, if electrons and holes have different mobilities, the higher mobility component will be more depleted from the generation zone. Hence it is expected that the electron and hole diffusion currents tend to cancel each other and minimize the net diffusion current. On the other hand,

the electron/hole drift currents add up to maximize the net drift current and proportional to the electrostatic potential gradient. Moreover, according to Onsager–Braun model, free carriers generation rate in organic semiconductors is strongly enhanced by an electric field [90, 91]. Finally, if a symmetric beam is used for excitation, the electron and hole concentration gradients will be equal around the centre of the beam and nulls the net diffusion current. Therefore, it is expected that the OBIC scan would generate a significant signal only in regions with an electrostatic potential gradient, i.e. a built-in electric field. In a p - n junction, the electrostatic potential varies along the depletion region, and it causes the OBIC signal to be significant there and to null in the neutral doped regions. It is possible to extract the electrostatic potential profiles from the OBIC profiles. However, this is not a trivial problem since the relationship is highly nonlinear. The details are beyond this text [92].

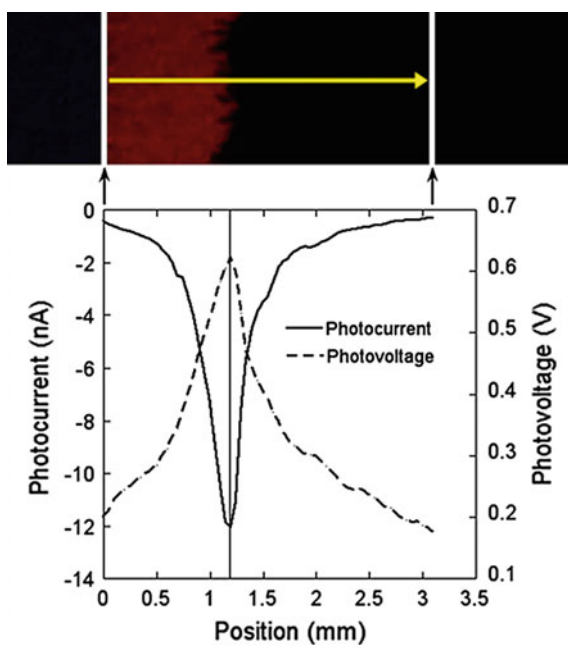
Compared to scanning electron beam or scanning Kelvin probe techniques, the OBIC method is simple to implement and widely used to characterize semiconductor junction structures and to map the minority carrier lifetime, defects, local resistance and cell uniformity of thin film solar cells. Application of the OBIC technique to an LEC was first reported by Dick et al [63]. A focused Argon laser beam was scanned across an encapsulated planar LEC approximately 20 μm wide mounted on a cooled scanning stage. V_{OC} , rather than I_{SC} , was measured to prevent rapid dedoping of the activated cell. The detection of a peak V_{OC} where the PL intensity showed a large step is consistent with the presence of a p - n junction. The width of the junction was estimated to be about 2 μm or 10% of the interelectrode gap. Since the activated device was only cooled to 250 K, well above the T_g of the electrolyte, the planar LEC was still prone to dedoping. The magnitude of the V_{OC} , at only a few tens of μV , was minuscule compared to the energy gap of the luminescent polymer. Since the I - V characteristics of a p - n junction are not linear, the V_{OC} profile would be different from the OBIC profile in width and shape. The challenges of optically scanning a fully frozen, small planar LEC in a cryogenic vacuum chamber (to avoid condensation) meant it was the only study of its kind in 15 years since its publication.

With the advent of extremely large planar LECs, we carried out several OBIC studies of planar LECs that are frozen in a vacuum cryostat. The frozen cells had an interelectrode spacing ranging from 700 μm to 4.6 mm. The extremely large gap size made it possible to use a variety of optical/cryogenic setups for added functionalities. The large planar cells were also easier to fabricate using shadow masking (versus photolithographic) techniques. In all these studies, the planar cells were activated at elevated temperatures, and cooled to 200 K or below to freeze the junction. In the remainder of this section, we briefly introduce the first two OBIC studies carried out in our lab. In Sects. 1.3 and 1.4, we describe in detail the latest OBIC/PL scans with a focused laser beam.

2.2.2 OBIC Scanning of Planar LECs with a Micromanipulated Cryogenic Probe Station

Hu and Gao turned on a 3.1 mm planar LEC in a micromanipulated cryogenic probe station (Janis ST-500) under vacuum [41]. The planar LEC had a composition of MEH-PPV (10):PEO(10):CsClO₄(3) in weight ratio and a pair of Au/Al electrodes deposited on top of the polymer film. The micromanipulated probes were used to make electrical contacts to the electrodes. The planar LEC was activated with a voltage bias of 300 V at 335 K. The cell current reached 3 mA and decreased when the cell was gradually cooled to 200 K to freeze the junction. The probe station was equipped with a fibre optical arm. The optical fibre was coupled to a 442 nm He-Cd laser beam and manually scanned across the entire interelectrode gap of the frozen planar LEC. OBIC scans were performed in both short-circuit and open-circuit conditions along the same path. Figure 2.8 shows the spatial OBIC and V_{OC} profiles of the scans along the path shown. Both profiles were very broad due to the large core diameter of the optical fibre used (200 μm) and the jaggedness of the junction. The depletion width of the junction, therefore, was not resolved. The OBIC and V_{OC} peaks, however, coincided precisely with the position of the p - n junction, shown above the scan profiles. The peak V_{OC} was over 0.6 V (versus a few tens of μV of the initial OBIC study), indicating a significant junction built-in potential.

Fig. 2.8 OBIC photocurrent and photovoltage profiles of a 3.1 mm frozen planar LEC measured in a Janis micromanipulated cryogenic probe station. *Top* the activated cell under UV illumination. The vertical white lines indicate the electrode/polymer film interfaces. The yellow line and arrow depict the scan path and direction. *Bottom* Photocurrent and photovoltage profiles for the scan path shown at the *top*. Reprinted from reference [41], Copyright (2011), with permission from Elsevier



2.2.3 Concerted OBIC and Scanning PL Imaging of Planar LECs with a Fluorescence Microscope

Subsequently, Inayeh et al. utilized a low profile microscopy cryostat and a fluorescence microscope to perform concerted PL and OBIC scans of planar frozen-junction LECs [42]. A schematic of this setup is shown in Fig. 2.9. The scanning optical beam was a focused beam of the mercury lamp attached to the fluorescence microscope. An octagon-shaped aperture was placed in the optical path. Moreover, the beam was focused to the surface of the planar LEC with a 40 $\times$ objective to a size of about 35 μm in diameter. This represented a significant improvement in scanning resolution compared to the probe station. Moreover, the setup allows for a simultaneous recording of the PL intensity of the film with the photodiode positioned below the cryostat. This configuration was made possible by

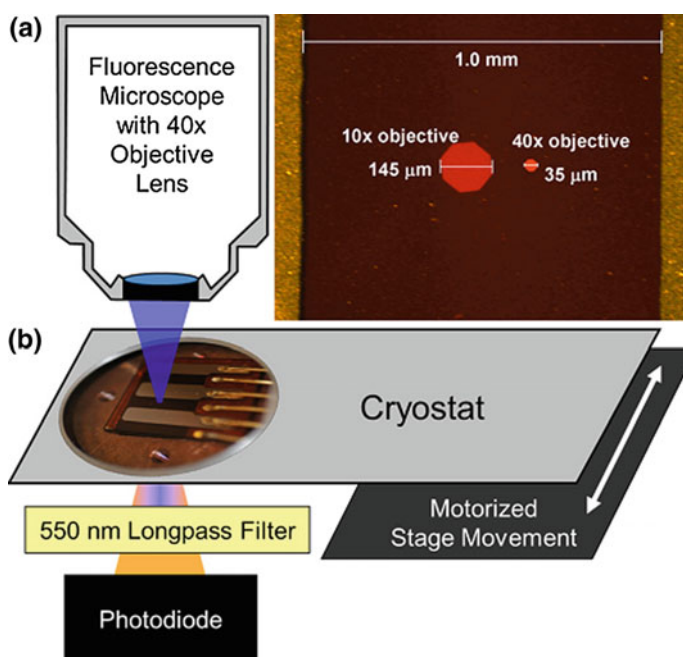


Fig. 2.9 *Top* Image of the undoped MEH-PPV:PEO:KTF planar LEC with a 1.0 mm interelectrode gap. Also shown are the illumination spots created using a 10 $\times$ objective lens and a 40 $\times$ objective lens. *Bottom* Schematic illustrating the experimental setup used to perform the OBIC and photoluminescence scans. Blue light (from 448 nm to 497 nm) originating from the mercury lamp is focused through a 40 $\times$ objective lens. The light travels through the cryostat window and excites the surface of the device. Unabsorbed blue light and photoluminescence from the LEC travel through the bottom window of the cryostat. A 550 nm longpass filter removes the unabsorbed blue light. The photodiode detects the photoluminescence intensity of the LEC film. The LEC is mounted in a microscopic cryostat and kept under vacuum. Reprinted with permission from reference [42]. Copyright (2012) American Institute of Physics

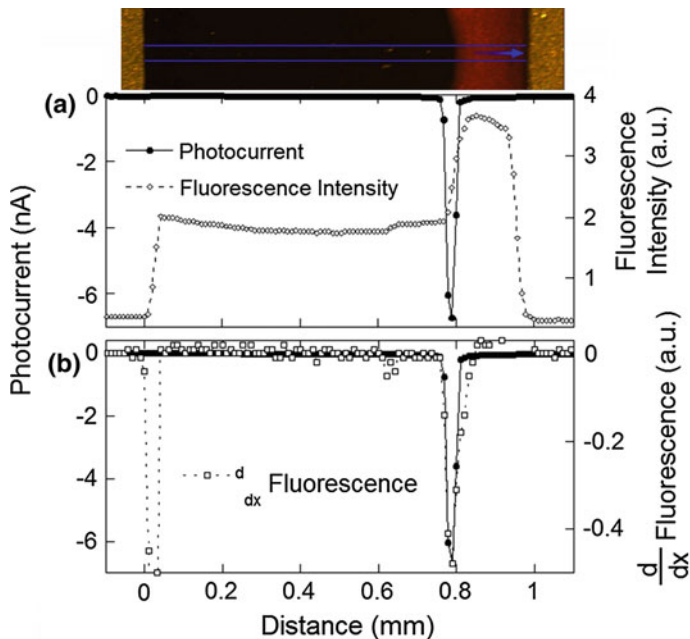


Fig. 2.10 OBIC photocurrent and photoluminescence intensity profiles of the frozen-junction cell shown in Fig. 2.2, an MEH-PPV:PEO:KTF planar LEC with a 1.0 mm interelectrode gap turned on with 25 V and cooled to 200 K. *Top* portion of the cell illuminated under *blue light* (the full cell is not illuminated during the OBIC scan). The *blue lines* depict the area of the cell exposed to light during the scan and the *blue arrow* indicates the direction of the scanning optical beam. *Middle* photocurrent and fluorescence intensity profiles of the scan path shown at *top*. *Bottom* photocurrent and differential change in fluorescence intensity profiles of the same scan path. Reprinted with permission from reference [42]. Copyright (2012) American Institute of Physics

the fact that the microscopy cryostat had both a top and a bottom optical windows, and the copper cold finger was partially hollowed out to let the light beam through. The beam was scanned across the cell by moving the cryostat which was mounted on a motorized scan stage with steps of 10 μm . Figure 2.10 shows the acquired OBIC and PL profiles from a 1 mm frozen-junction planar LEC. Even without the photograph shown at the top, we can easily observe that the OBIC peak is located at the junction region, where the PL intensity underwent a sharp transition. Detailed analysis, however, revealed that both the PL transition region and the OBIC peak had a width comparable to the beam width. This indicates that the beam was still not narrow enough to resolve the depletion width of the frozen junction. Further improvement to the scanning resolution was needed.

2.3 OBIC and Scanning PL Probing of a Frozen Planar *p-i-n* Junction

2.3.1 Introduction

In Sect. 2.2, we introduced the OBIC technique as a valuable tool to probe the electronic structure of planar LECs. Dick et al. first demonstrated the feasibility of measuring the spatially resolved V_{OC} and PL intensity across a planar LEC, although the LEC studied was not fully frozen, nor was the photocurrent measured [63]. The invention of extremely large planar LECs makes the OBIC technique extremely attractive due to their ease of fabrication and compatibility with various scanning apparatus. Our group's first two attempts at scanning extremely large planar LECs were successful in that (1) the cells were sufficiently cooled to freeze the LEC junction. (2) the OBIC was measured for the first time as well as the V_{OC} . The latter was on the order of the built-in potential expected, and (3) the OBIC and PL signals were obtained concurrently. The PL trace provides a reliable reference for determining the position of the OBIC peak relative to the junction position. The results showed that the peak OBIC and V_{OC} occurred at the junction. The polymer/electrode interfaces and much of the neutral doped regions were not photovoltaic-active. These studies described briefly in Sects. 2.2.2 and 2.2.3, however, did not resolve the depletion width of the LEC junction due to the limitation of the scanning apparatus. The beam size in the second study was about 35 μm , so it was interesting to note that the increase in the gap size of the planar cell did not lead to a wider depletion width that scales with the size of the planar cell. To improve the scanning resolution, the second scanning setup was modified and employed to scan a unique planar polymer *p-i-n* junction [43]. For the first time, the depletion width of a planar LEC junction has been resolved from a scanning optical measurement. This section describes in detail the experimental setup and the obtained results.

2.3.2 Experimental Details

A planar LEC with a 700 μm gap size was fabricated on a 15 mm $\times$ 15 mm 1 mm sapphire substrate inside a nitrogen-filled glovebox/evaporator system. The LEC film was spin cast from a cyclohexanone solution of MEH-PPV, PEO and potassium triflate (KTf) with a weight ratio of 10:5:1.2 and subsequently dried for 5 h at 50 $^{\circ}\text{C}$. After that, aluminium electrodes with a thickness of 100 nm were deposited on top of the LEC film under a vacuum of $\sim 1.5 \times 10^{-6}$ torr. The finished planar LEC had an active area of 8 mm by 700 μm . The planar LEC was loaded into a microscopy cryostat, sealed and transferred out of the glovebox for testing.

The scanning OBIC/PL apparatus again consists of a Nikon fluorescence microscope and a motorized scanning stage onto which the cryostat is mounted. In addition, a Keithley-237 source measurement unit was used to supply the voltage bias and simultaneously measure the device current during both the activation and the scanning processes. A photodiode recorded the PL intensity of the cell during the scan, and the cell temperature was controlled via a Cryocon 32 controller. The measurement was controlled with a custom LabView program. These arrangements are similar to the last OBIC/PL scan. The optics of the scanning setup, however, had been changed. Instead of focusing down the beam of the attached mercury lamp, the lamp assembly was removed from the microscope. A single mode He-Cd laser (442 nm) was used as the light source. Mirrors and a 6.5/1.1 Galilean telescope were used to steer and expand and elevated the laser beam. A plano-convex lens with a focal length of 15 cm was used to couple the beam into the microscope's rear aperture. The dichroic mirror inside the microscope directed the laser beam into a 10 $\times$ objective and focused it onto the device under test through the cryostat optical window. The 2D beam profile was captured using the CCD camera mounted on top of the microscope. The 1D intensity profile of the scanning beam was obtained by integrating the 2D profile perpendicular to the scanning direction. The resulting profile fits well to a Gaussian with a $1/e^2$ waist diameter of $\sim 13\text{ }\mu\text{m}$, about 1/10 of the size of the focused lamp beam using the same 10 $\times$ objective.

2.3.3 *Resolving the Depletion Width of a Planar p-i-n Junction*

The 700 μm planar LEC was activated by applying a voltage bias of 150 V. The cell temperature was kept at 325 K for about 250 s and subsequently increased to 330 K to speed up the activation process. When the device current had reached about 1.3 mA ($t = 850\text{ s}$) the flow of liquid nitrogen was turned on to cool the device at a rate of -0.365 K/s until the device reached 200 K. The device was illuminated with a 365 nm wavelength UV lamp during the activation process. The time-lapse fluorescence images of the cell are shown in the top part of Fig. 2.11. Like the large planar cells shown in Figs. 2.5 and 2.6, in situ electrochemical doping, manifested as PL quenching, was again highly visible under UV illumination. The doped regions expanded until the doping fronts met and the EL of the cell started to grow stronger. Cooling led to a dimmer and red-shifted EL at $t = 1300\text{ s}$. The last image in the second row was taken at 200 K with the 150 V bias removed. A significant observation was a bright line between the p - and n -doped regions. This is different from the frozen cells shown in Figs. 2.8 and 2.10. The bright line has stronger PL than the neighbouring p - and n -doped regions and is a less quenched quasi-intrinsic region. Therefore, the doping profile of this planar cell is that of a p - i - n junction.

The focused laser beam was scanned across the frozen planar LEC with a step size of 1 μm , in a direction that was perpendicular to the p - i - n junction. Each scan

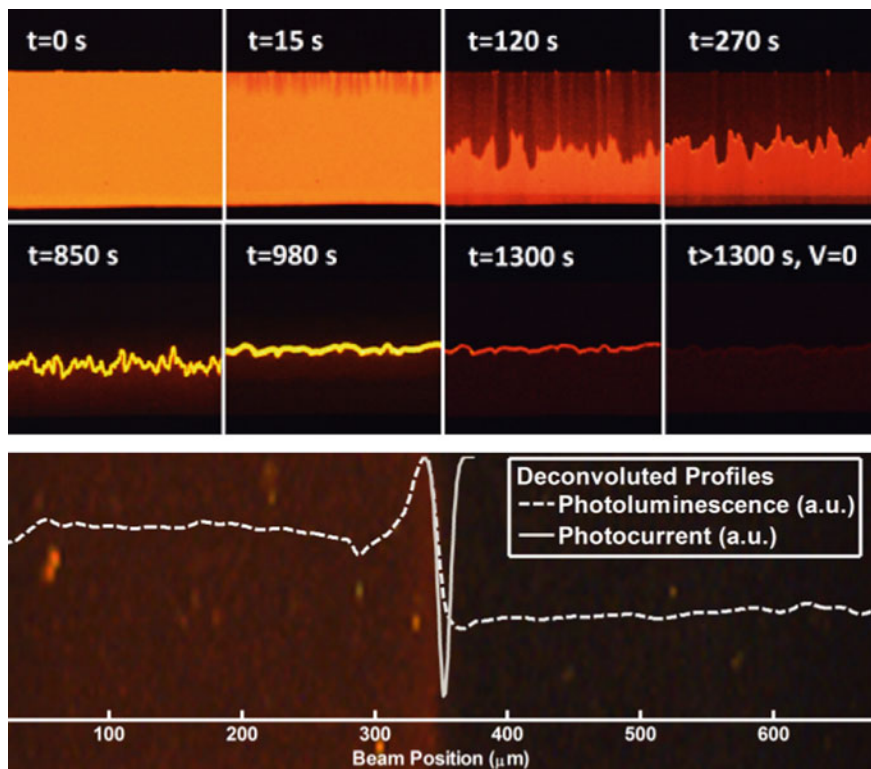


Fig. 2.11 *Top* device snapshots during the turn-on and freezing process. The *top* electrode (anode) was positively biased relative to the lower electrode (cathode). The *p*-doped region at the *top* is visibly darker than the *n*-doped region in the lower part of the film. Only 1,100 μm by 700 μm of the entire device active area is shown. *Bottom* Deconvoluted photocurrent and PL profiles. The background in the lower panel shows the frozen LEC pictured at zero bias. The scan was done along the central horizontal line in the figure. The UV lamp was turned off. Reprinted with permission from reference [43]. Copyright (2015) WILEY-VCH Verlag GmbH & Co

generated a set of raw OBIC and PL profiles. Since the scanning laser beam had a significant size of about 13 μm in diameter, deconvolution was necessary to extract the true OBIC/PL profiles. This was done by fitting the measured PL and OBIC peaks to separate Gaussian functions. The Gaussian laser beam was then deconvoluted from these fitting functions. The deconvoluted OBIC and PL curves are shown in the lower part of Fig. 2.11. The photocurrent peak has a $1/e^2$ width of ~ 18 μm . The PL peak, on the other hand, extends over a wider area.

Since the exciton diffusion length in PPVs is on the order of nm, the width of the deconvoluted OBIC peak is a good approximation of the width of the depletion region. We note that the PL profile indeed includes a prominent PL peak in the junction region. Also, the OBIC peak is displaced by about 12 μm to the right, close to the *i/p* interface. It is reasonable to assume that the peak OBIC position is

also the position of the peak built-in field. The most significant discovery of this study is the determination of the depletion width of a planar, frozen polymer junction. Moreover, the LEC junction has the doping profile of a $p-i-n$ junction. Manzanares and Heeger first discussed the possibility of a $p-i-n$ junction in a polymer LEC. A majority of the doping profiles observed in extremely large planar LECs, however, have been those of a $p-n$ junction. These as-formed $p-n$ junctions can relax into a $p-i-n$ junction. The OBIC profile of a $p-n$ junction, as well as a partially relaxed $p-n$ junction, is described in the next section.

2.4 High-Resolution OBIC and Scanning PL Imaging of a Frozen Planar Polymer $p-n$ Junction

2.4.1 Introduction

The ultimate goal of a scanning optical measurement, when applied to planar LECs, is to uncover the inner electronic structure of the LEC junction that is responsible for all of LEC's functionalities as either a light-emitting device or a photovoltaic cell. To achieve this goal, the scanning resolution must be sufficiently high compared to the features to be resolved. The scanning setup described in Sect. 2.3 produced a scanning beam of about 13 μm in diameter. While it was sufficient to resolve the depletion width of a planar $p-i-n$ junction, the beam diameter is still too large compared to what is obtainable within the diffraction limit. We note that in the first OBIC study by Dick et al. the laser beam was focused to have a diameter of about 1 μm with the use of a 40 $\times$ microscope objective [63]. A high-powered objective, however, could not be used in the previous setup as it led to a second focused spot on the device surface. This was likely caused by some internal reflections of the laser beam which entered the microscope from the lamp port. In this section, we describe a revised optical scanning setup that has overcome this problem. The focused beam had a Gaussian shape with a $1/e^2$ width of only 1.9 μm . The planar LEC itself had also been optimized by fine-tuning the LEC blend, the electrode material and the operating conditions. The planar LEC was activated to exhibit a straight, long and highly emissive $p-n$ junction that had been successfully frozen. The concerted, high-resolution OBIC and scanning PL imaging the frozen planar LEC exposed the narrowest $p-n$ junction in a frozen LEC ever reported [44].

2.4.2 Experimental Details

The planar LECs in this study had a composition of MEH-PPV (10): PEO (5): KTF (1.2) by weight and a thickness of about 0.5 μm . A pair of thermally evaporated gold electrodes defined a 700 μm interelectrode spacing and a cell length of 7 mm.

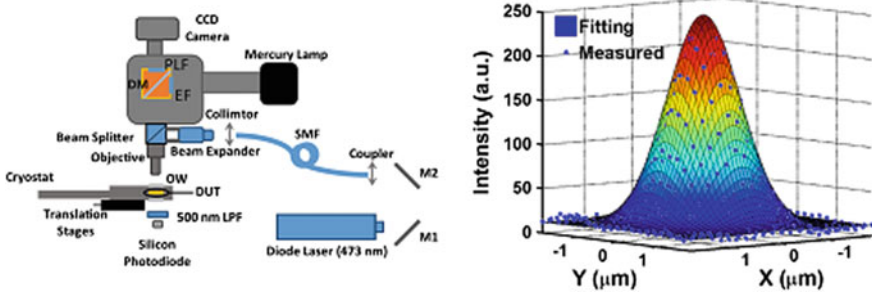


Fig. 2.12 *Left* Experimental setup for scanning OBIC and PL imaging of frozen planar LECs. *Right* 2D beam profile and Gaussian fit of the focused excitation beam. Reprinted with permission from reference [44]. Copyright (2016) American Institute of Physics

The same microscopy cryostat was used to house the cell, and the device fabrication and testing procedures are identical to those described in Sect. 2.3.2. The light source and optics have been modified. The experimental setup is shown in Fig. 2.12. A blue single mode diode laser (473 nm) was used as the excitation source. The laser beam was steered using mirrors (M1, M2) and coupled into a single mode fibre (SMF) via a coupler lens. Another lens was attached at the other terminal of the fibre to collimate the output beam which was then expanded in size. A 50/50 beam splitter cube then redirected the beam into a 50 $\times$ objective and at the same time allowed light collected by the objective to pass through. This arrangement allowed the excitation beam to by-pass the microscope optics. In addition, the mercury lamp was reattached which was used to take fluorescence images of the cell during activation. The focused Gaussian beam had a $1/e^2$ width of 1.9 μm at the device surface. A silicon photodiode positioned under the bottom optical window collected the PL from the LEC film. The excitation beam was rejected by a low-pass filter (LPF) with a cut-off wavelength of 500 nm, between the optical window and the photodiode. The device PL pictures were captured via a 10 $\times$ objective using a CCD camera that is mounted on top of the microscope. This provided a field of view that covers an area of 0.9 mm $\times$ 1.8 mm.

2.4.3 Results and Discussion

The planar LEC 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/s to 170 K. The lower freezing temperature of 170 K compared to 200 K used in previous scans ensured a fixed junction for multiple optical scans. The frozen junction was verified by repeated I - V scans, which did not show change over the course of the experiment. The top panel of Fig. 2.13 depicts the cell geometry and the time evolution of cell current and cell temperature during the activation process. We note that a very high

peak current of over 5 mA had been reached, which is an indication of strong doping and good film quality. The lower panel displays the time-lapse fluorescence images of the cell. The LEC film is uniformly fluorescent before the voltage bias was applied ($t = 0$ s). The doping fronts of this cell propagated much faster than the earlier cells shown in Sects. 2.2 and 2.3. At $t = 3$ s, a large part of the LEC film was already doped to either p -type on the anode (+) side or n -type on the cathode (−) side. At $t = 9$ s, a continuous light-emitting p - n junction was visible between the doped regions. The p - n junction was initially very uneven but became much straighter with time. Meanwhile, the doped regions became darker, indicating an increase in doping level. The darkening of the LEC film was accompanied by the rapid increase in cell current. The applied voltage bias was removed once the target temperature of 170 K had been reached. The PL image of the frozen cell revealed a p - n junction doping profile. A thin bright line was observed in the junction region. However, the intensity of the bright line was not high enough to suggest a p - i - n junction structure. Moreover, it will be shown that the as-activated p - n junction could be relaxed into a p - i - n junction when subjected to warming/re-cooling cycles.

A total of 18 OBIC/PL scans were performed across the frozen p - n junction as seven locations. Figure 2.14 shows the OBIC and PL profiles of a full

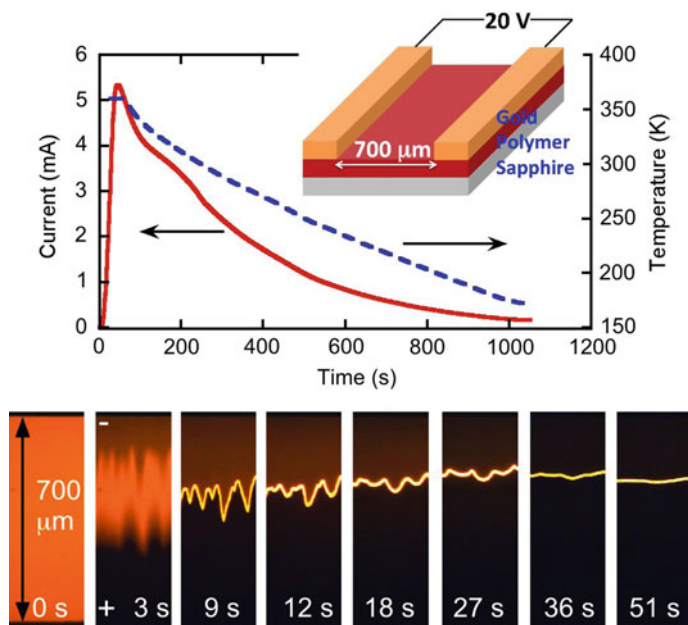
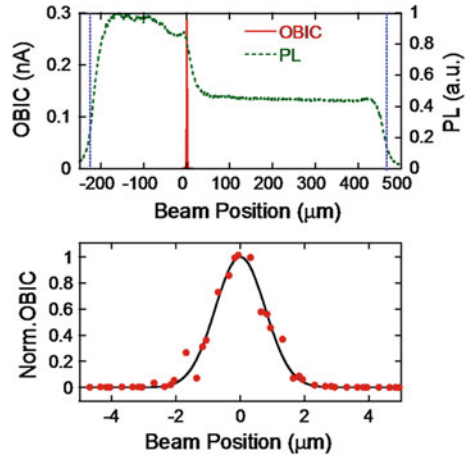


Fig. 2.13 Device activation process. *Top* Time evolution of the cell current and temperature during the activation process. A DC voltage bias of 20 V was applied. The inset shows a schematic of the planar LEC. *Bottom* Time-lapse fluorescence images of the planar LEC during the activation process. Only a section of the entire cell is shown. The *bright line* formed after $t = 9$ s is due to electroluminescence of the cell. Reprinted with permission from reference [44]. Copyright (2016) American Institute of Physics

Fig. 2.14 OBIC and PL profiles of the frozen planar LEC across the same junction region. *Top* Full OBIC and PL scans of the planar LEC across the entire planar LEC. The cathode is located at $-230\ \mu\text{m}$ and the anode is located at $470\ \mu\text{m}$, as indicated by the vertical dashed lines. *Bottom* OBIC data of four scans and Gaussian fit to the data near the OBIC peak. Reprinted with permission from reference [44]. Copyright (2016) American Institute of Physics



(electrode-to-electrode) scan. The OBIC peak was assigned a beam position of zero μm as a reference. The PL profile indicates an n -doped region with the highest overall PL intensity and a darker, p -doped region to the right of the OBIC peak. A small local PL peak just to the left of the OBIC peak can be attributed to the thin bright line observed in the PL image. The sensitivity of the PL scan is evident in the detection of a PL “transition zone” on the p side of the junction, between 0 and $+30\ \mu\text{m}$. In this zone, the PL intensity decreased continuously from the high level of the n side to the much lower level of the p side. The large variation in PL intensity is also visible near both electrode interfaces. This variation indicates a large doping gradient, and the level of doping is the highest just inside the electrode edges, for both p - and n -doped films. This observation is consistent with the results of the contact probing measurement.

The most significant observation is the extremely narrow and prominent OBIC peak at $x = 0\ \mu\text{m}$. The lower panel of the figure provides an expanded view of the OBIC peak that incorporated the data points from a total of four scans across the same junction region. The data points of the individual scan were adjusted/shifted so that their peak positions coincide. This procedure was necessary to eliminate any offset due to the mechanical hysteresis of the scanning stage. The data are fitted to a Gaussian function, from which a $1/e^2$ width of $3.1\ \mu\text{m}$ was determined. Since both the scanning beam and the measured OBIC profile are Gaussian functions, deconvolution also results in a Gaussian whose width is given by $\sqrt{W_{OBIC}^2 - W_{Beam}^2}$, where W is the $1/e^2$ Gaussian width. The deconvoluted OBIC peak width is $2.45\ \mu\text{m}$. We note that all 18 scans yielded an OBIC peak width that was larger than the excitation beam diameter of $1.9\ \mu\text{m}$. An average of all 18 scans gives an OBIC width of $2.53\ \mu\text{m}$ with a standard deviation of $0.45\ \mu\text{m}$. The average OBIC peak width after deconvolution is $1.5\ \mu\text{m}$. The average OBIC signal is $292 \pm 40\ \text{pA}$ for an excitation beam intensity of $2\ \mu\text{W}$.

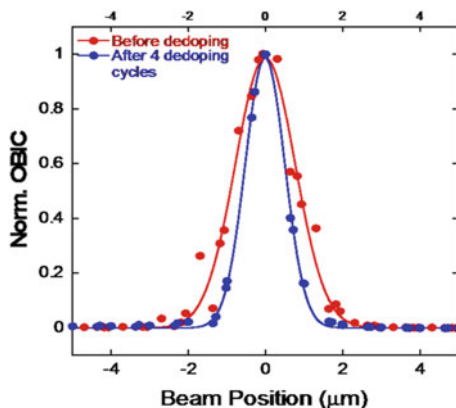
Since the exciton diffusion length in MEH-PPV is on the order of nm, the OBIC peak width should represent the junction depletion width. The average junction width of 1.5 μm is the smallest ever measured in a planar LEC, regardless of the interelectrode spacing. The junction width accounts for a mere 0.21% of the interelectrode gap, which is the lowest value reported for LECs. The OBIC junction width is also much smaller than the width of the EL zone ($\sim 10 \mu\text{m}$) and the PL transition zone ($\sim 30 \mu\text{m}$). The small junction width obtained attests to the high resolution of the scans.

The drop-off in PL intensity to the right of the OBIC peak indicates a doping gradient at the edge of the p - n junction. There is a strong possibility that the doping gradient is caused by the presence of rough features on the sub-micrometre scale. Sharp protrusions on a larger scale had been observed along a planar p - n junction [80]. They contributed to a tunnelling leakage current that degraded the rectification ratio of the as-formed frozen p - n junction. The sharp features, however, could be removed by subjecting the frozen p - n junction to a warming/cooling cycle that caused partial dedoping and smoothing the p - n junction. The “relaxed” p - n junction exhibit improved rectification and a much larger V_{OC} when illuminated.

In an attempt to smooth out the junction and eliminate any possible submicron protrusions the frozen cell was partially relaxed after the aforementioned scans. The relaxation/dedoping cycle was carried out by briefly (for a few minutes at a time) warming the frozen cell to 260 K and cooling it back to 170 K. During these thermal cycles, the cell was kept at an open-circuit condition to avoid fast dedoping and the loss of the active junction. In total, four relaxation cycles were carried out. The cell current decreased after each cycle, and the I - V curves became more nonlinear and less symmetric.

This is a strong indication that dedoping had occurred. OBIC scans were performed after each dedoping cycle along the same junction location. As the cell became more resistive, the input optical power was increased to obtain a measurable OBIC signal. Figure 2.15 compare the normalized OBIC profiles without dedoping and after the final dedoping cycle. The measured OBIC profile narrowed to $\sim 2 \mu\text{m}$ after dedoping. After subtracting the beam width, the junction width is only 0.6 μm compared to 2.45 μm without dedoping. A very prominent PL peak appeared to the left of the OBIC peak. The PL profile became similar to that of a p - i - n junction shown in Fig. 2.11. The p - i - n junction formed by controlled dedoping, however, is quite different from an as-formed p - i - n junction discussed in Sect. 1.3. Here, the removal of the fine features along the edge of the junction resulted in the narrowest OBIC peak ever reported for a planar LEC. The p - i - n junction had sharp boundaries between the differently doped regions. Indeed, the PL transition region between the “ i ” region and the p region has narrowed to about 3 μm from nearly 30 μm in the as-formed p - n junction. The more abrupt PL transition is consistent with a narrowed OBIC profile and a reduced junction width.

Fig. 2.15 Normalized OBIC scans at the same location before and after four dedoping cycles. The excitation laser power used was 2 μW (red) before dedoping and 50 μW (blue) after four dedoping cycles. Reprinted with permission from reference [44]. Copyright (2016) American Institute of Physics



2.5 Conclusion and Outlook

Polymer-based LECs are intriguing and promising devices that offer attractive device characteristics not easily attained by other organic electronic devices. Doping plays an essential role in the operation of polymer-based LECs. On one hand, doping leads to conductivity increase that gives LECs their desirable electrical properties. On the other hand, the optical effect of doping allows for the visualization of the dynamic doping process via time-lapse fluorescence imaging. In this chapter, we summarized our recent experimental work on the scanning optical imaging of planar LECs. The experiments exploited both the electrical and optical effects of doping, as well as the temperature dependence of ionic conductivity of the LEC film. For the first time, we had resolved the junction depletion width of a planar *p-i-n* junction and a planar *p-n* junction. The narrowing of the junction upon thermal cycling strongly suggests the presence of fine structures on the edge of the junction. For an as-formed, frozen *p-n* junction, the depletion width accounted for only 0.2% of the entire cell area enclosed by the electrodes. Since only the junction region contributes to EL and PV response in an LEC, the narrow junction width is not ideal for efficient operation of LECs as either a light-emitting device or a PV cell. An igneous solution to this problem is to form multiple junctions that are simultaneously emitting without increasing the total cell area. By introducing dispersed, metallic particles to the LEC film, we successfully demonstrated a new device structure called a bulk homojunction (BHoJ) LEC [93–96]. A BHoJ planar LEC exhibits vastly improved effective emitting area as well as a giant V_{OC} when operated as a PV cell. BHoJ LECs in a sandwich configuration and frozen at room temperature represent a major challenge and opportunity in LEC research.

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