Decoding the polymer p-n junction: controlled de-doping and reverse bias electroluminescence

D. Wang, E. Desroche, and J. Gao*

Department of Physics, Engineering Physics and Astronomy, Queen's University

Abstract

Semiconductor junctions are at the heart of many semiconductor devices from the simplest diodes to high performance transistors and photonic devices. Among devices based on a doped p-n or p-i-n junction, the polymer light-emitting electrochemical cell (PLEC) is a unique solid-state device possessing attractive attributes for low-cost applications, but also a junction structure that is still poorly understood. In a PLEC, the p-n junction is formed by applying a voltage bias between the contacts of the device. The applied voltage causes *in situ* electrochemical p- and n-doping of the semiconducting polymer and the formation of a dynamic light-emitting p-n junction. Once the junction is fixed by cooling or chemical manipulation, the “frozen-junction” PLEC exhibits an unipolar electroluminescence (EL) and photovoltaic response. Repeated thermal cycling, however, can cause the frozen-junction PLEC to experience drastically enhanced EL under forward bias and the emergence of reverse bias EL. In this study, we use a combination of transport measurements and direct imaging to elucidate the origin of the mysterious reverse bias EL. We develop a model that explains the reverse bias EL as caused by the tunnel injection of electrons and holes from band gap states into a de-doped “intrinsic” region between the p- and n-doped regions. The model explains the location, relative intensity and evolution of EL under both forward and reverse bias. The results strongly hint at a junction that is much narrower than previously resolved.

* Email: jungao@queensu.ca

Introduction

Solid-state lighting and high information content displays are in high demand in our society striving for energy efficiency. The revolution in lighting and display technologies coincided with major breakthroughs in the development of light-emitting diodes (LEDs), which can be made with both group III-V inorganic semiconductors and various organic compounds. Organic LEDs, or OLEDs, are now widely used in high-end cell phone displays and TV monitors.

LEDs are electroluminescent (EL) devices. EL can be classified into many sub-types based on excitation modes, charge carriers, or energy states involved.¹ Commercial LEDs employ various junction structures to optimize the injection, transport, and confinement of charge carriers as well as the out-coupling of emitted photons. LEDs exhibit diode rectification due to the presence of these unipolar metal/semiconductor, homo- or hetero-junctions within the devices. Reverse biasing an LED typically does not cause significant current flow nor light emission. This is also true for the simplest OLED consisting of a homogenous light emitter layer contacted by two dissimilar electrodes.²

One notable exception to unipolar emission is the light-emitting electrochemical cell, or LEC.³ The first LECs were made of organic polymers: a light-emitting polymer (LEP) and a solid polymer electrolyte (SPE) are mixed to create an active layer that is a mixed ionic/electronic conductor. Even with two dissimilar electrodes, the polymer LEC (PLEC) exhibits nearly identical current and EL under both forward bias (FB) and reverse bias (RB).⁴ Moreover, these PLECs display low threshold voltages and high efficiencies comparable to those of unipolar PLEDs made with the same LEP.^{5, 6} The highly unusual device characteristics of LECs are attributed to an *in situ* electrochemical doping process that can occur regardless of the biasing polarity. The simultaneous p- and n-doping of the LEP creates a p-n junction that emits light due to the injection of minority charge carriers. The LEC p-n junction is dynamic. That is, removing the voltage bias causes the p-n junction to dissipate and reversing the biasing polarity can form a new light-emitting p-n junction of the opposite polarity in a different location of the cell.

Historically, LECs were invented to address the major drawbacks of OLEDs—namely the use of reactive metal electrodes for electron injection and an ultrathin active layer prone to shorts between the electrodes. In these aspects, the LECs have succeeded spectacularly. This is

evidenced by the demonstration of planar, or lateral (vs. sandwich) PLECs with a separation of over 10 mm between a pair of identical aluminum electrodes.⁷ Time-lapse photoluminescence (PL) and EL imaging of the highly emissive planar PLECs allowed for the direct visualization of the electrochemical doping and junction formation processes.

LECs have yet to achieve the commercial success of OLEDs due to their generally inferior response speed and operational lifetime, both trade-offs brought on by the doping process itself. The operational stability of LECs has been steadily improving due to innovations in materials and better understanding of LEC mechanisms.⁸⁻¹³ In addition to PLECs,¹⁴⁻¹⁶ the latest LECs have emitters that include organic small molecules,¹⁷⁻¹⁹ ionic transition metal complexes²⁰⁻²⁴, host-guest materials,^{25, 26} and perovskites.^{27, 28}

In LECs, the doping is not permanent because the counter-ions for doping are mobile as opposed to being embedded in a crystal lattice. In SPEs, ion transport ceases at temperatures below the glass transition temperature (T_g), which is slightly above 200 K for polyethylene oxide (PEO)-based SPEs. To immobilize the counter-ions, one can simply cool the LEC after junction formation. This leads to frozen-junction LECs that exhibit fast response time and unipolar light emission.²⁹⁻³¹ Frozen-junction LECs can also be realized chemically by using high T_g electrolytes or other innovative ionic materials.³²⁻³⁷

In a frozen-junction LEC, EL is only observed under FB since reversing the biasing polarity can no longer reverse the doping structure of the cell at temperatures below T_g . Temporally heating the unbiased cell to above T_g , however, can significantly alter the device performance when the LEC is re-frozen.³⁸ The heating/cooling cycle, when controlled carefully for duration and heating temperature, can cause dramatic increase in EL intensity and decrease in cell current. These changes are attributed to the partial de-doping of the LEC in the junction region, which creates a p-i-n junction that is more resistive but also more emissive due to much reduced quenching of the LEP in the “intrinsic” (i) region.

The partial de-doping of the frozen p-n junction also causes the emergence of EL under a large reverse bias (RB), which is the subject of this study. The cause of this anomalous RB EL has remained a mystery since its first discovery more than a decade ago. Why is the RB EL only observed in a partially de-doped frozen p-i-n junction, but not in the as-frozen p-n junction despite a much higher RB current of the latter? Since the p-i-n junction is frozen, the formation of a new junction by doping reversal is ruled out. “Hot” carrier EL is unlikely due to the low

charge carrier mobility and large bandgap of the LEP. Moreover, the RB EL is observed under vacuum, so process such as electro-photoluminescence that relies on the partial breakdown of air is ruled out. In this study, we carried out comprehensive experimental investigations of the RB EL in multiple devices underwent repeated heating/cooling cycles. Direct imaging confirmed that the RB EL, albeit much weaker, occurred in the same junction region as FB EL. We develop an injection-based model to explain the onset and progression of RB EL, a long-standing mystery of the polymer p-i-n junction. The model also allowed for, for the first time, the quantitative analysis of the current vs. voltage (I-V) characteristics of a frozen junction to distinguish the various conduction regimes.

Methods

The 0.6 mm planar PLECs of this study were fabricated in an integrated glovebox/evaporator system filled with circulating dry nitrogen gas. The luminescent polymer used was poly[5-(2'-ethylhexyloxy)-2-methoxy-1, 4-phenylene vinylene] (MEH-PPV). The polymer electrolyte consisted of poly(ethylene oxide) (PEO) and potassium trifluoromethanesulfonate (KTf). The MEH-PPV, PEO and KTf were dissolved in cyclohexanone with concentrations of 1%, 2% and 5% (w/v), respectively. Suitable amounts of these master solutions were mixed together to create a casting solution with a weight ratio of MEH-PPV:PEO:KTf=1:1.3:0.25. The solution was spin-cast onto a glass substrate to form the active PLEC layer. The coated glass was then heated at 50°C for 5 hours on a hot plate to remove any residual solvent from the polymer film. Subsequently, aluminum electrodes 100 nm in thickness was thermally evaporated onto the polymer film through a shadow mask to complete the device.

The finished PLEC was mounted in a microscopy cryostat inside the glove box. A small bead of thermal paste was applied between the glass substrate and the copper cold finger of the cryostat. The cryostat was then sealed and transferred to an optical table for testing under a Nikon fluorescence microscope. Prior to testing, the cryostat was put under vacuum with an oil-free mechanical pump and the cell was heated to a preset temperature of either 310 K or 335 K via a Cryocon 32B temperature controller. A cryogen transfer line connected the cryostat and a liquid nitrogen (LN) dewar. The cooling system was pressurized to induce LN flow while the preset temperature was maintained. A UV ring light was positioned atop the cryostat quartz

window for imaging. For EL intensity measurement, an amplified Hamamatsu photodiode was used to cover the entire quartz window of the cryostat. Relative EL intensity was read out as a voltage with a Keithley 2010 multimeter. The PLECs were powered with a Keithley 237 high voltage source measure unit, controlled by a custom LabVIEW program that allowed for temperature control, cell activation, and current vs. voltage vs. EL scans. A digital camera mounted on top of the Nikon microscope recorded images directly to a PC.

Results

In this section, we present detailed results obtained from two planar PLECs. The two cells were nominally identical but activated differently before cooling. Figure 1 shows the time evolution of cell current, EL, and cell temperature of Cell A during activation and cooling. The cell was heated to 335 K before a constant voltage bias of 15 V was applied. The voltage bias caused the cell current to increase exponentially starting at $t \approx 6$ s and to reach 0.5 mA at $t=33$ s when cell cooling commenced. The current overshoot to 1.05 mA before finally decreased at $t=56$ s when cell temperature dropped to 324 K. The increase in cell current from the initial value of 1.3 μ A by nearly three orders of magnitude is the direct result of electrochemical doping and junction formation. The p-n junction first formed at $t \approx 6$ s, which led to the onset of EL and the exponential “turn-on” of cell current at the same time. Both EL and cell current continued to increase as the level of doping increased until the temperature drop caused both to decrease. It took approximately 5 min for the cell temperature to reach the pre-set value of 200 K. A wait period of 60 s was applied before the voltage bias was removed. The plateaued cell current and EL indicate that the cell temperature had stabilized and the cell was frozen.

Figure 1. The activation of Cell A. Cell A was heated to 355 K before a constant bias voltage of 15 V was applied. Cooling of the cell to 200 K commenced at $t = 33$ s when EL peaked. The curves show time evolution of cell current, EL and cell temperature.

The as-frozen Cell A was characterized at 200 K by current-voltage-EL (I-V-EL) scans. Subsequently, Cell A underwent five heating/cooling cycles between 255 K and 200 K. After each of these cycles, the cell was re-tested at 200 K. Figure 2 displays the effects of these cycles. Figure 2(a) compares the I-V and EL-V characteristics of the cell before and after the first de-doping cycle, which lasted 1 min at 255 K. The as-frozen Cell A had a symmetric I-V curve about zero bias. After cycle one, the cell current under RB decreased significantly. EL, which was only observed under FB in this -5 V to 5 V scan, increased by several folds despite a measurable decrease in FB current. Figure 2(b) shows the change in the I-V curves as more de-doping cycles were applied. With each additional cycle, the cell current decreased and the I-V curves became less linear. The cell developed diode rectification due to a larger drop in RB current than FB current. Figure 2(c) displays the EL-I curves for FB. The de-doping cycles caused the FB EL to become stronger and more efficient. Under FB, EL is a linear or slight sub-

linear function of cell current. Finally, Figure 2(d) reveals RB EL that appeared after cycle one and grew stronger with each additional de-doping cycle. Under RB, EL exhibit a super-linear dependence on cell current. Overall, RB EL is more than two orders of magnitude weaker than FB EL measured at the same current.

Figure 2. FB and RB I-V-EL characteristics of Cell A before and after de-doping cycles. All tests were carried out at 200 K. In cycle one, the cell was heated to 255 K and held for 1 min before cooling back to 200 K. The hold times for cycles 2-5 are 1 min, 2 min, 2 min and 5 min, respectively. These times do not include the time it took to ramp up and ramp down the cell temperature. (a) I-V and EL-V curves before and after cycle one. (b) I-V curves. (c) EL-I curves for FB EL. (d) EL-I curves for RB EL.

A second planar PLEC, Cell B, was also activated and frozen. A voltage bias of 100 V was applied at a cell temperature of 310 K. Cell cooling commenced when the cell current reached 0.13 mA at $t=120$ s. The cell was cooled to 200 K after about 6 min. Cell B activated in this manner was far more resistive than Cell A. Nevertheless, Cell B exhibited very similar behavior as Cell A both before and after the heating/cooling cycles were applied. Figure 3(a) shows the I-V curves of Cell B taken between -300 V and 300 V. The large voltage bias of 300 V was necessary to reach appreciable cell currents, shown as positive values for both FB and RB. The as-frozen Cell B exhibited an I-V curve that is completely symmetric about zero bias and linear. The cell current decreased with each additional de-doping cycles, and the I-V curves

became less symmetric and developed pronounced curvature. Figure 3(b) shows the same data in a semi-log form for the range between -100 V and 100 V. The I-V curves became more diode like with each de-doping cycle. Figure 3(c) and Figure 3(d) display the respective EL-I curves for FB and RB. Once again, we observe that the de-doping cycles caused the EL to increase and the emergence of RB EL. Although still weak compared to FB EL, the RB EL of Cell B exhibited strong super-linear dependence on current and was much stronger than the RB EL of Cell A.

Figure 3, FB and RB I-V-EL characteristics of Cell B before and after de-doping cycles. All tests were carried out at 200 K. The hold times and heating temperatures for the various de-doping cycles are indicated in the graphs. The de-doping cycles began with 1 min at 255 K and ended after 2 min at 275 K. (a) I-V curves in linear form (b) I-V curves in semi-log form (c) EL-I curves for FB EL. (d) EL-I curves for RB EL.

The PLECs of this study are planar (lateral) cells with a very large separation between the two parallel electrodes. This allowed for the direct imaging of any changes caused by the de-doping cycles, as shown in Figure 4 for Cell A. Figure 4(a) shows the PL image of the as-frozen Cell A without bias. The dark, heavily PL-quenched p-doped region occupied a slightly larger portion of the inter-electrode gap of 0.6 mm. Below the p-doped region, a partially quenched n-

region exhibited the characteristic red PL of MEH-PPV. The junction between the p- and n-doped regions is not straight but smooth. Figure 4(b) shows the PL of Cell A after de-doping cycle five. The image appeared to be slightly brighter, but there was no perceivable change to the junction region. Figure 4(c) shows the FB EL of an as-frozen Cell A under a constant driving current of +0.2 mA. The image was taken under room light to reveal the electrodes but without any UV illumination. The thin red line tracing the exact location and shape of the p-n junction is the FB EL. Figure 4(d) shows the FB EL of Cell A after de-doping cycle five. The image was taken under the same exposure and lighting conditions, except that the driving current was halved to +0.1 mA. It is easy to see that de-doping caused significant enhancement of the FB EL, confirming the results of Figure 2(c). Figure 4(e) captures the RB EL of the de-doped Cell A. The image was taken in the dark under a constant current of -40 μ A. Albeit faint even after image enhancement, the RB EL is visible in the same junction region that gave rise to FB EL.

Figure 4. PL and EL images of Cell A as frozen and after de-doping cycle five. (a) PL image of an as-frozen Cell A under UV illumination without bias. (b) PL image of Cell A after de-doping cycle five imaged under identical conditions as in (a). The brightness and contrast of the PL images in both (a) and (b) were enhanced by applying the same LEVEL adjustment in Photoshop®. (c) FB EL of an as-frozen Cell A under a constant driving current of +0.2 mA. The image was taken under room light to reveal the electrodes but without any UV illumination. (d) FB EL of Cell A after de-doping cycle five. A constant current of +0.1 mA was applied. EL images in (c) and (d) were taken under identical conditions. These images were not enhanced. (e) RB EL of the de-doped Cell A after cycle five. The image was taken in the dark under a constant current of -40 μ A. The image was enhanced by applying LEVEL adjustment in Photoshop®. The cell was cooled to 200 K for all images.

Figure 5. PL and EL images of Cell B as frozen and after the last de-doping cycle at 275 K for 2 min. (a) PL image of an as-frozen Cell B under UV illumination without bias. (b) PL image of Cell B after the last de-doping cycle imaged under identical conditions as in (a). The brightness and contrast of the PL images in both (a) and (b) were enhanced by applying the same LEVEL adjustment in Photoshop®. (c) FB EL of an as-frozen Cell B under a constant driving current of +10 μ A. The image was taken under UV illumination. (d) FB EL of Cell B after the last 275 K de-doping cycle. A constant current of +5 μ A was applied. EL images in (c) and (d) were taken under identical conditions without any enhancement. (e) RB EL of the de-doped Cell B after the last 275 K de-doping cycle. The image was taken in the dark under a constant current of -3 μ A. The image was enhanced by applying LEVEL adjustment in Photoshop®. The Cell was cooled to 200 K for all images.

PL and EL images were also acquired for Cell B. Figure 5(a) and Figure 5(b) show the before and after PL images of Cell B. The as-frozen p-n junction in Figure 5(a) is highly jagged in comparison to the smooth junction of Cell A. The de-doped Cell B in Figure 5(b) developed a thin bright region between the darker p- and n-doped regions. The as-frozen p-n junction had relaxed into a p-i-n junction. Figure 5(c) shows the as-frozen Cell B driven by a FB current of +10 μA , imaged under UV illumination. FB EL takes the shape of the jagged p-n junction. Figure 5(d) shows Cell B after de-doping driven by a FB current of +5 μA . By comparing the images of Figure 5(c) and Figure 5(d), we observe significant enhancement of FB EL after de-doping, despite a halved driving current. By comparing Figure 5(b) and Figure 5(d), we observe the FB EL is originated from the i region of the p-i-n junction. Finally, Figure 5(e) reveals RB EL of the de-doped Cell B imaged in the dark. Albeit faint and appearing broken, the RB EL can be once again attributed to the same frozen junction region that gave rise to the FB EL.

Discussion

In the preceding Results section, we presented the I-V and EL-I characteristics, along with PL and EL images of two frozen cells before and after multiple de-doping cycles were applied. The planar cells were activated differently. Cell A was activated by applying a relatively low bias voltage of 20 V at a cell temperature of 335 K. Cell B was activated with a 100 V bias at a lower temperature of 310 K. The low voltage/high temperature and high voltage/low temperature activations are both commonly used in extremely large planar PLECs.³⁸⁻⁴² The former typically resulted in a smoother junction, while the latter gave rise to a very jagged but highly emissive junction that is also easier to control due to a slower doping process. Here, we used both activation schemes to achieve two frozen cells that differ significantly in cell resistance and junction smoothness. We emphasize that the results of Cell A and Cell B are repeatable. Their differences in cell current and junction smoothness are caused by the operation parameters, not by device-to-device variations. Through many trials, we determined the duration and temperature at which the cell could be de-doped to effect measurable differences in transport and emission properties. We found that the higher conductance of Cell A allowed it to be de-doped at 255 K. While additional de-doping cycles at up to 275 K were applied to Cell B. Remarkably, both cells exhibit the same trends in their I-V and EL-I characteristics as well as significant EL enhancement upon de-doping. More important, de-doping led to RB EL in both

cells in the same region as the FB EL. The results suggest the RB EL is a universal phenomenon independent of cell activation conditions and junction morphology.

(i) *Device model*

In order to find the common cause of the RB EL, we focus on the fact that RB EL is only observed when the frozen cell is de-doped. The difference between an as-frozen cell and a de-doped cell is that of a p-n vs. a p-i-n junction. Figure 6(a) shows the distributed resistances of the as-frozen cell as well as its energy band diagram under RB. The thin red region in the middle schematic represents the depletion region of a p-n junction. Both Cell A and Cell B exhibit a RB current as large as the FB current, despite the presence of a unipolar p-n junction. Moreover, the I-V curves are mostly linear. The linear I-V curves indicate that the cell current became limited by the series resistances of the p- and n-doped regions- $R_{\text{junction}} \ll R_p + R_n$. From the FB current at +20 V and +300 V, the limiting resistances of the as-frozen Cell A and Cell B are determined to be 106 k Ω and 21 M Ω , respectively. At $|V| < 3$ V, the cell current exhibits significant curvature that can be attributed to the p-n junction. This is shown in Figure S1 for Cell A. We note that $I_{\text{RB}} > I_{\text{FB}}$. At a 1 V bias, I_{RB} is approximately an order of magnitude higher than I_{FB} . At low voltages, the most likely cause of a large reverse junction current is a tunneling current.⁴³ As shown in the energy band diagram, an electron in the valence band on the p-side can directly tunnel through the narrow junction region reaching the conduction band on the n-side, leaving behind a hole. Since the tunnel-injected electrons and holes are majority carriers upon crossing the junction, EL is not generated. The tunneling mechanism described is typically observed in a p-n junction of high levels of doping on both p- and n-sides.⁴³ This is the case for an as-frozen junction when the doping level is the highest. At higher RB, the tunneling current became limited by the series resistances of the cell and gave rise to the linear, symmetric I-V curves observed in the as-frozen p-n junctions.

Figure 6. Junction schematics and energy band diagrams representing an as-frozen PLEC and a de-doped PLEC under RB. (a) Distributed resistances, junction schematic, and energy band diagram of a p-n junction. R_p denotes the series resistance of a neutral p region, R_n is the resistance of a neutral n region. R_{p-n} is the junction resistance due to the depletion region. E_{cp} , E_{vp} , E_{cn} , E_{vn} represent the top and bottom conduction band and valence band for the p- and n-doped regions. (b) Distributed resistances, junction schematic, and energy band diagram of a p-i-n junction. R_{p-i-n} is the junction resistance. 1, 2, 1' and 2' represent injections of electrons (solid circle) and holes (open circle) from various energy levels across the intrinsic region. (c) Simplified energy band diagram of a p-i-n junction under RB showing charge injection from band gap states E_{FP} and E_{FN} . $e\phi_1$ and $e\phi_2$ are the heights of injection barriers.

Figure 6(b) shows the resistances, junction structure, and band diagram of a de-doped cell, which is modeled as a p-i-n junction. The emergence of a highly resistive i region easily explains the decrease in the overall current under both FB and RB with each de-doping cycle, as shown in Figure 2(b) and Figure 3(a). At large FB voltages, the I-V curves are still well represented by a linear function even after de-doping. The limiting resistances of Cell A and Cell B, after the last de-doping cycles, are determined to be 403 k Ω and 87 M Ω , respectively. Thus, the limiting resistances had quadrupled after the final de-doping cycles. By comparison, the change in junction resistance is far greater. Figure 3(b) showed that at -50 V, the resistance of Cell B decreased by nearly *four orders of magnitude*. This gave rise to a current rectification ratio of $I(+50 \text{ V})/I(-50 \text{ V})=72$ due to a relatively smaller decrease in FB current. We deduce that

the junction resistance R_{p-i-n} became much greater than $R_p + R_n$. This led to the observed diode rectification. The drastic decrease in current at low RB voltages is due to a diminished tunneling current as the tunnel barrier became thicker with the emergence of an i region.

Nevertheless, RB current became significant under a large RB and caused the emergence of RB EL in the same i region as FB EL. This is shown in the energy band diagram of Figure 6(b). Note that only electron and hole injected from the band edges E_{vp} and E_{cn} , denoted by 1 and 1', can have the required spatial overlap for possible recombination. Any electrons and holes injected between the band edges do not have the any immediate spatial overlap and will be driven further apart by the applied electric field. A more probable cause of the RB EL is the injection of electrons and holes from band gaps states, as shown in the processes denoted 2 and 2'. Here, the injected charge carriers will be driven toward each other, increasing the likelihood of radiative recombination. These band gap states could be due to structural defects or impurities inherent to the LEP. More likely, they are polaronic or bipolaronic states brought on by the doping process.⁴⁴ In electrochemically doped MEH-PPV, these band gap states are responsible for PL quenching and the emergence of additional absorption bands in the longer wavelength regions.

In Figure 6(c), these band gaps states are collectively represented by the levels labelled E_{Fp} and E_{Fn} . Under RB, large potential energy barriers $e\phi_1$ and $e\phi_2$ exists for the injection of electrons and holes. Under FB, the injection barriers of $E_g - e\phi_1$ or $E_g - e\phi_2$ are much smaller. This explains the diode rectification of the de-doped cell. We note that the band diagram of Figure 6(c) is essentially that of a single-layer polymer LED (PLED) under RB. The levels E_{Fp} and E_{Fn} are analogous to the Fermi levels of two dissimilar electrodes. To inject an electron from E_{Fp} into the CB of the intrinsic region, a large triangular potential energy barrier must be overcome via either tunneling (denoted 1) or thermionic emission (denoted 2). Likewise, the injection of holes involves a similar triangular energy barrier. With dual injection of electrons and holes, RB EL occurs as a result of radiative recombination.

(ii) *Charge injection analysis*

At 200 K, we believe the dominating injection mechanism at large RB is tunneling. Fowler-Nordheim (FN) tunnelling describes the injection of electrons through a triangular potential energy barrier.⁴⁵ If we ignore the effect of barrier lowering due to image force, the FN tunneling current takes the form of $I \propto F^2 e^{-\kappa/F}$, where I is cell current, F is electric field, κ is a

parameter that depends on the barrier height and electron effective mass. A plot of $\ln(I/F^2)$ vs. I/F should yield a straight line. A plot of $\ln(I/V^2)$ vs. I/V is generated for Cell B, where I is cell current in mA and V is the total applied RB. Figure 7 shows that after the last de-doping cycle, data at large RB values (150 V to 300 V) can be fitted to a perfect straight line ($R^2 > 0.999$). Therefore, FN tunneling is a highly probable cause of current injection under these conditions. When the cell is less de-doped, a linear fit between $\ln(I/V^2)$ and I/V is not possible at the largest RB voltage values due to a resistance-limited current (i.e., the I-V curve is a linear function). A linear $\ln(I/V^2)$ vs. I/V fit, however, exist for an intermediate range of voltage values, as shown in Figure 7. We note the onset voltage for FN tunneling shifted higher with additional de-doping. The deviation from the FN behavior at lower RB values had been assigned to thermionic emission in a similar analysis of PLEDs.⁴⁵

Figure 7. Fowler Nordheim plots for Cell B after de-doping cycles at 265 K and 275 K. The solid red markers represent data used to generate the linear fits.

Under FB, charge injection occurs over much smaller potential barriers. At low bias voltages, the data fit very well to the model of field-assisted thermionic emission (TE).⁴⁶ This is shown in Figure 8 for Cell B. The highlighted data points in solid red show linear dependence between $\ln(I)$ and $V_{1/2}$, as prescribed by the model. The same data points also fit well to an

exponential function between I and V . This steep, exponential “turn-on” in current is commonly observed in LEDs under FB above a threshold voltage that is related to the built-in potential of the diode.⁴⁵ Figure 8 shows the built-in potential of the de-doped cell is on the order of 1-2 V. This value is deduced from the voltage value above which the $\ln(I)$ vs. $V_{1/2}$ curve is a straight line, as shown by the solid circles in Figure 8. Note the as-frozen curve is skewed due to significant leakage current at $V < 1$ V. This leakage current was effectively removed by de-doping. At large FB, the current is once again resistance-limited.

Figure 8. $\ln(I)$ vs. $V_{1/2}$ plots for Cell B under FB. The solid red markers represent data used to generate the linear fits.

The FN and TE analysis of I - V curves have also been applied to Cell A, which exhibited the same behavior, as shown in Figure S2. These results establish that in de-doped cells the current flow under a large RB is mainly due to FN tunneling. While under a low FB, the current flow is due to field-assisted thermionic emission. Figure 9(a) shows EL vs. voltage characteristics of Cell B under RB. From the semi-log plots the threshold voltages for RB EL are determined to be 150 V, 100 V, ~ 50 V and ~45 V for the de-doping cycles shown. These values match almost perfectly to the onset voltages of FN tunnelling current extracted from Figure 7 for the same de-doping cycles, which are 150 V, 105 V, 45 V and 40 V, respectively. Figure 9 (b) shows EL vs. FB voltage curves for the same de-doping cycles. Here, all four curves show a threshold voltage

for FB EL of less than 20 V. This is once again consistent with the low onset voltages for significant thermionic current flow under FB. We note that for both RB and FB, the EL is shown to decrease with additional de-doping cycles in these EL-V plots. This is due to a drastically decreased cell current as the cell is de-doped. When measured at the same injected current, the EL was vastly enhanced with de-doping, as shown in Figures 2 and 3.

Figure 9. EL vs. V plots for Cell B for RB (a) and FB (b). To generate the semi-log plots, a constant in the range of 0.0002-0.0012 was added to the individual curves to remove the negative readings caused by background noise.

The above analysis led to the conclusion that different current injection mechanisms are responsible for RB EL and FB EL in these frozen cells. FN tunneling is responsible for EL under a large RB, while field-assisted TE accounts for the FB EL with a very low threshold voltage. The very different injection mechanisms explain key differences between FB EL and RB EL. In the junction model presented in Figure 6, we did not consider any local variation in junction curvature, doping concentration, junction width, and barrier height. These variations must exist and explain the intensity fluctuations observed along the long junctions. In regions where the junction is either too narrow or too broad, RB EL does not occur or is too faint to be imaged. Since FN tunneling is highly sensitive to electric field and barrier height, any local variation in junction curvature and potential barrier height might cause injected electrons and holes to follow slightly different paths towards the other side of the i region. This reduces their chance of recombination and explains why the RB EL is 1~2 orders of magnitude lower in intensity than FB EL at the same injected current. The weak RB EL suggests radiative recombination of

injected electrons and holes is a “side effect” of current flow. In this case, the injection-limited EL can exhibit a super-linear dependence on the injected current,⁴⁷ as shown in Figure 2(d) and Figure 3(d). Under FB, the frozen cells behave similarly to a FB-based OLED with much smaller injection barriers. The “bimolecular” recombination of injected electrons and holes leads to a linear EL vs. I characteristics, as shown in Figure 2(c) and 3(c).

(iii) *Estimation of injection barriers*

The junction and injection model presented above can explain the shape of the I-V-EL curves as well the origin of RB EL. For a FN tunneling current, I , driven by an applied electric field, F , the slope of the linear $\ln(I/F^2)$ vs. $1/F$ fit is: $\kappa = 8\pi\sqrt{2m^*}\varphi^{1.5}/3eh$, where m^* is electron effective mass, h is planck’s constant, e is elementary charge, and φ is energy barrier height (e ϕ in Figure 6). In order to extract the injection barrier height, we need to know the width of the i region so that F can be calculated. Optical-beam-induced-current (OBIC) imaging of a similar p-i-n junction by our group revealed a junction width of 0.6 μm .⁴⁰ In OBIC imaging, a focused laser beam is scanned across the lateral device structure and the resulting photocurrent is recorded as a function of location. Since photocurrent is only generated in regions where a built-in field exists, the junction depletion width can be inferred from the measured OBIC profile. The 0.6 μm junction width represented the smallest value ever resolved for a planar PLEC and accounted for less than 0.1% of the inter-electrode spacing. A junction width on the order of μm , however, does not lead to realistic estimates of the injection barrier height.

Assuming the entire applied voltage bias was dropped across a 0.6 μm i region and taking m^* as the free electron mass m_0 , Cell A yielded a barrier height of only 0.08 eV after the last relaxation cycle. For Cell B, a barrier height of 0.31 eV was calculated. Both values are too small for a cell under RB depicted in Figure 6(c). Even smaller values are calculated for cells that were less de-doped due to the smaller slopes of the FN fit. Since the de-doped planar PLECs can have an open-circuit voltage on the order of E_g , a large built-in potential must exist and a more realistic value for φ should be on the order of 1 eV or higher. A narrower junction will result in a larger and more realistic injection barrier value.

Barrier width estimate also supports the notion of a narrower junction. For a 150 V bias across the 0.6 μm i region, the field strength would be 2.5×10^6 V/cm. For a realistic barrier height of 1.5 eV, this would lead to a barrier width of 6 nm, which is too wide for any significant tunneling current. These estimates suggest that the real junction width could be much smaller.

This might explain why the effect of de-doping cannot be discerned by comparing the PL images in Cell A. For Cell B, the bright i region is highly visible, but it might not be a simple, uniform region of low doping. The fact that the de-doped Cell A and Cell B exhibit the same trends in cell current and EL, despite their very different macroscopic features, suggests an unresolved narrow junction region might be responsible for their many common device characteristics. Further studies are needed to gain insight into the finer doping structures of the de-doped LEC junctions.

Conclusions

In this study, we investigated the electrical and EL characteristics of frozen LEC junctions subjected to repeated thermal cycling which caused partial de-doping of the junctions. In particular, the RB EL of a de-doped LEC junction was elucidated. The RB EL had been observed in two planar PLECs that were activated under very different conditions. For both devices, direct imaging confirmed that the RB EL, albeit much weaker, occurred in the same junction region as the FB EL. Although only visible in Cell B, we believe the emergence of an intrinsic region is responsible for the drastic changes observed in current flow and EL in both devices. An injection-based model was developed to explain the onset and progression of RB as well as the I-V curves of the frozen polymer p-i-n junction. Under FB, the dual injection of electrons and holes over a small potential energy barrier resulted in a large current flow and EL at a very low bias voltage. The dominating injection mechanism is field-assisted thermionic emission. Under reverse bias, electrons and holes are injected via Fowler-Nordheim tunneling into the i region over a much larger potential energy barrier. Using junction width obtained from the OBIC scans, we estimate the height of injection barriers. The results strongly hint at a junction that is much narrower than that resolved by scanning photocurrent imaging.

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