Prevention of Short Circuits in Solution-processed OLED Devices

Pinholes in the emitting layer of an Organic Light Emitting Diode (OLED), e.g. induced by particle contamination or processing flaws, lead to direct contact between the hole-injection layer (HIL) and the cathode. The resulting short circuits give rise to catastrophic device failure. We demonstrate that these short circuits can be effectively prevented by an oxidative treatment of the HIL with aqueous sodium hypochlorite (\(\text{NaClO}_{(aq)}\), bleach), which locally lowers the conductivity of the HIL (i.e. PEDOT:PSS) by more than eight orders of magnitude while leaving the emitting layer virtually unaffected. The oxidizer treatment is evidenced by an order of magnitude reduction in leakage current and strong reduction in the number of bright spots in the emitting area, without affecting the device lifetime. Diode behavior is even recovered in deliberately flawed devices containing 80 micron sized defects.

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4.1 Introduction

As explained in the previous chapters, it is a major challenge in the production of OLEDs to prevent defects that induce undesired current pathways. Such leakage currents limit device efficiency and may develop into “hard” short circuits during operational lifetime, sometimes causing catastrophic device failure due to the high local current density and concomitant steep rise in temperature in the shorted region.

Current leakage paths and short circuits occur both outside and inside the active emitting device area. The former may occur in the bus-bar or contact region at the edge of the device, bypassing the organic semiconducting layers, whereas the latter are typically a result of incomplete coverage of the hole-injection layer (HIL) or anode by the light-emitting polymer (LEP) layer, allowing direct local contact between cathode and anode (see Figure 4.1B). We have described several causes for small pinholes in the LEP layer in chapter 2.3 such as shadow effects around trapped particles during thermal evaporation or spin coating, or local de-wetting of the LEP solution after wet deposition. Alternatively, defects can also comprise conducting particles (e.g. metal dust or ITO spikes) that bridge anode and cathode directly, penetrating both organic layers (defect “2” in Figure 4.1B). The defects described above can be specified as extrinsic defects that can be reduced by processing the LED under proper cleanroom conditions.

In Figure 4.1C, however, a defect is shown that cannot be prevented by clean working environment: the commonly used PEDOT:PSS forms agglomerates with dimensions larger than the typical LEP film thickness (∼100 nm) that protrude through the LEP layer. Such a defect then causes a direct contact between HIL and anode, leading to local short circuits. It is a significant challenge to prevent or repair this kind of intrinsic short circuits.

In this chapter a novel and facile repair procedure is proposed based on submersion of the OLED stack (substrate/ITO/PEDOT:PSS/LEP) in an aqueous oxidizing solution prior to cathode deposition. Sodium hypochlorite (NaClO(aq)) is used as an oxidizing agent known to effectively disrupt the conductivity of PEDOT:PSS via over-oxidation of the thiophene rings (see chapter 2 and 3). Hence, this treatment is expected to cancel the detrimental effect of defects characterized by local exposure of the organic HIL.

In the previous chapter we systematically investigated the effect of hypochlorite treatment on single PEDOT:PSS layers. We showed that a hypochlorite concentration of 5 wt% guarantees complete disruption of the conductivity of a 100 nm thick PEDOT:PSS layer on time scales of the order of seconds, without considerable removal or dissolution of material. In this chapter we use this information to find treatment conditions allowing local deactivation of PEDOT:PSS without negatively affecting the LEP layer. The repair procedure is tested on devices which were artificially defected by selective local removal of LEP using laser ablation. Quantification of the repair procedure is obtained by comparing defected devices with intact reference OLEDs in terms of their current-voltage characteristics. In a final experiment the oxidative repair method is applied to devices which have not been deliberately defected, in order to demonstrate the compatibility of the procedure with “real-life” OLED production.
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Figure 4.1: A) Schematic cross section of a standard bottom-emitting polymer-based OLED. B) Schematic representation of common causes for short circuits in the active device area: local absence of LEP (1), bridging particles (2), and protruding PEDOT:PSS agglomerates (3). C) FIB-SEM cross section of an OLED defect based on a large PEDOT:PSS agglomerate (defect 3 in Figure 4.1B). In this particular case silver (applied by thermal evaporation) is used as anode and the platinum layer has been deposited as part of the FIB-SEM procedure.
4.2 Materials and methods

An aqueous dispersion (0.84% solids) of PEDOT:PSS was supplied by AGFA Gevaert (Mortsel, Belgium) and used as received. Additional information on the type of PEDOT:PSS used in this work has been reported in chapter 3. White and blue LEP was purchased from Merck KGaA (Darmstadt, Germany). NaClO\textsubscript{(aq)} solution (reagent grade, available chlorine 4.00-4.99%) was purchased from Sigma-Aldrich and diluted with de-ionized water to concentrations of 0.005 % to 5% by weight.

Pre-patterned glass substrates (152×152 mm) containing nine ITO pixels (23×22 mm) were subsequently cleaned with detergent solution, rinsed with demi-water, and treated with oxygen plasma. PEDOT:PSS was spin-coated directly after plasma treatment and subsequently annealed for 10 minutes at 200 °C in a vacuum oven to give a dry layer with a thickness of 100 nm. The plates were allowed to cool down to 20 °C, after which the LEP was spin-coated from toluene on top of the PEDOT:PSS to give a dry layer with a thickness of 80 nm. The substrates were transported to a vacuum chamber (P < 5 × 10\textsuperscript{-7} mBar), where (nominally) 5 nm barium and 100 nm aluminum were consecutively applied in a co-evaporation procedure. After cathode deposition, the substrates were encapsulated with a metal lid to prevent oxidation by water and oxygen.

Artificial short circuits were created by ablating holes (d\textsubscript{hole} = 80 or 800 µm) in the LEP layer using a pulsed excimer laser operating at \( \lambda = 248 \text{ nm} \). The laser power settings and pulse frequency were tuned as to selectively remove the LEP while leaving the underlying PEDOT:PSS layer mostly unaffected. Selective local ablation of LEP was verified by profilometry using a Veeco Dektak 6M stylus profilometer.

Treatment with NaClO\textsubscript{(aq)} was performed by fully submerging the substrates in NaClO\textsubscript{(aq)} solution (at concentrations in the range 0 – 5 wt% for photoluminescence (PL) measurements and 5% for defect repair) for a specified duration (i.e. 5 seconds to 2 hours for PL measurements and 30 seconds for short circuit healing). The samples were subsequently rinsed with de-ionized water for ten seconds in order to remove excess hypochlorite. The samples were then dried under a nitrogen flow followed by cathode deposition and encapsulation.

The current – voltage (J/V) characteristics of defected, treated, and reference devices were measured in air with a Keithley 2440 source meter. PL measurements were performed on glass-based samples comprising an 80 nm thick white LEP layer on top of a 100 nm PEDOT:PSS layer using an Edinburgh FLSP920 series luminescence spectrophotometer.

4.3 Results and discussion

In order to investigate to what extent the LEP material is affected by treatment with aqueous sodium hypochlorite, we first performed photoluminescence (PL) measurements on treated layers of white LEP. Glass-supported PEDOT:PSS-LEP stacks were immersed in NaClO\textsubscript{(aq)} solutions with concentrations in the range 0 – 5 wt% for durations in the range 0 – 2 hours. Figure 4.2 shows the subsequently recorded PL-spectra ((A) crude, and (B) normalized). Figure 4.2A shows that for a treatment time below 10
minutes a decrease in PL intensity of only ~10% was observed, irrespective of hypochlorite concentration. It is however noted that the presented spectral data is merely qualitative, and has not been corrected against a calibration standard. As a consequence, sample-to-sample PL intensity fluctuations of ~10% coincide with the inherent accuracy of the equipment.

Only for prolonged treatment times, i.e. typically exceeding 15 minutes, the PL intensity decreases considerably, most likely due to chemical degradation of the LEP by hypochlorite. The retarded effect for treatment times below 10 minutes may be ascribed to the considerable difference in polarity between the aqueous environment and the rather hydrophobic LEP. Consequently, fast swelling and plasticization of the polymer matrix is avoided, which suppresses diffusion and reaction rates of hypochlorite ions. Therefore, for short treatment times, the LEP remains seemingly unaffected. In contrast, we have shown in the previous chapter that complete loss of electrical conductivity of the much more hydrophilic PEDOT:PSS layer is already achieved after one minute submersion time in 5 wt% NaClO\textsubscript{aq}. The relative changes in the PL spectrum of the white LEP at long treatment times, emphasized by the normalization of the spectra relative to the emission peak at $\lambda = 456$ nm (Figure 4.2B), may be due to differences in reactivity with hypochlorite between the various emitting entities present in the polymer.

A systematic investigation into the transient stages of chemical degradation of the various monomers of the LEP is certainly of interest from a fundamental perspective but lies outside the scope of this chapter. Instead, we emphasize that the present results, in combination with our previous investigations,(see chapter 3) show that an immersion time $<10$ minutes of a PEDOT:PSS-LEP stack in 5 wt% NaClO\textsubscript{aq} allows ample opportunity to fully disrupt the conductivity of exposed PEDOT:PSS in defected areas without significantly affecting the luminescent properties of the LEP layer. What’s more, as also shown in the previous chapter, a short treatment time would allow for complete disruption of the local conductivity, but without removal of the reaction product. In other words, under

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those conditions a residual layer of insulating material is likely to remain, which is likely to limit direct contact between the cathode and the ITO anode.

Systematic investigation of the repairing capability of a NaClO\textsubscript{aq} treatment in areas where the PEDOT:PSS layer becomes exposed ideally requires control over the occurrence of potentially short circuiting defects. For this reason we resorted to controlled local laser ablation of LEP from prior processed device stacks, rather than relying on the random character of "naturally" occurring events during wet processing. The power and pulse settings of the laser (excimer, $\lambda = 248$ nm, see Materials and methods section) were adjusted to achieve selective removal of LEP material without considerably affecting the underlying PEDOT:PSS layer. The selectivity of the process was verified by measuring cross-sectional height profiles of the PEDOT:PSS-LEP stack in and just outside the ablated area, whereby a scalpel was used to locally scratch away residual material at the bottom of the crater (Figure 4.3). The graph indeed confirms that a patch of LEP was removed with high selectivity from an 80 nm thick integral layer covering a 100 nm thick PEDOT:PSS layer. After ablation, the local thickness of the PEDOT:PSS layer had reduced by $\sim 10\%$, illustrating that we locally ablated the LEP and stopped slightly below the PEDOT:PSS-LEP interface. Other features in the profile, i.e. the elevation at $x \sim 200$ $\mu$m and the "spikes" at $x = 500$ and 600 $\mu$m, can be respectively ascribed to re-deposition of ablated LEP material and buckling around the scratch trace.

We ablated relatively large areas of LEP ($d \sim 800$ $\mu$m) for the sole purpose of easy visual inspection and crater profiling. However, in order to controllably create defective device samples for studying repair by hypochlorite treatment we also ablated much smaller areas ($d \sim 80$ $\mu$m) to achieve better resemblance with processing-induced "real life" random defects. In order to confirm that the ablation of an 80 $\mu$m hole in the LEP layer indeed leads to a short circuit upon cathode deposition, the optical and electrical characteristics of the deliberately defected devices were monitored by measuring the light output (electroluminescence (EL)) and the current density ($J$) as a function of voltage ($V$).\textsuperscript{[10–15]}

Figure 4.4A compares the JV-characteristics of an exemplary device containing a laser-
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Figure 4.4: A) Current density ($J$) plotted as function of voltage ($V$) for an OLED in which a hole ($d = 80 \mu m$) was ablated in the LEP prior to cathode deposition (red), and for an intact reference device (black). Inset: magnified EL photograph of the ablated defect and surrounding area. B) Current density ($J$) plotted as function of voltage ($V$) for an hypochlorite treated OLED with an ablation crater in the LEP (blue) and for the same reference device as in A (black). Inset: magnified EL photograph of the ablated and hypochlorite-treated defect and surrounding area.

The perforated LEP layer (red) with an intact reference device which was not deliberately defected (black). The graph clearly reveals very different behavior for these two cases. The reference device neatly exhibits the "classical behavior" characterized by a low leakage current ($J < 10^{-2}$ mA/cm$^2$) at negative and low positive bias ($|V| < 2.5$ V), followed by a turn on and charge injection regime at $V > 2.5$ V. In contrast, the deliberately defected device has a three orders of magnitude higher leakage current and complete loss of rectification, as shown by the symmetry in the red JV curve. Nevertheless, despite the significantly altered electrical characteristics, the shorted devices still produced light. Close inspection of the illuminating area in the vicinity of the ablated hole (inset of Figure 4.4A) reveals the presence of a corona with increased light intensity around the ablated region (visible as a dark hole), most likely caused by a high local current density.

Figure 4.4B shows the comparison of the JV-characteristics of the best performing reference device (black) with a device which was intentionally defected and subsequently treated for 30s with 5% NaClO$_{aq}$ (blue). Strikingly, the treated device shows full "recovery" of the classical shape of the JV-curve, clearly exhibiting rectifying behavior and a leakage current which is even somewhat lower than that of the reference device. This result demonstrates that the NaClO$_{aq}$ treatment completely deactivates the short circuited region and allows the repaired OLED to operate normally. Close inspection of the active area in the vicinity of the repaired defect (inset figure 4.4B) shows that the bright spot has been "removed", owing to the absence of high local current density due to disruption of the PEDOT:PSS conductivity, so that only the ablated region remains (visible as a black spot). We note that the seemingly lower light output of the treated OLED compared to the untreated one, as suggested by the insets, is solely due to difficulties in obtaining proper EL photographs and not to the hypochlorite treatment itself. Furthermore, the recovery of a low leakage current and normal device characteristics confirms the expectation that...
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Figure 4.5: A) Current density (J) as plotted function of voltage (V) for 43 OLED devices, of which 28 devices were treated with 5% NaClO\textsubscript{(aq)} for 30 s (blue) and 15 left untreated (black). Insets 1 and 2 respectively show typical EL photographs (low magnification) of the active area of an untreated OLED and an OLED treated with aqueous hypochlorite. The brightness and contrast of these photographs was modified to improve the visibility of the bright and black spots; B) Luminance (L) plotted as a function of voltage (V).

there is no cathode-LEP interface effect and that the cathode indeed remains electrically insulated from the ITO anode after oxidative repair with hypochlorite solution.

These results show that a 30s treatment with 5 wt% aqueous hypochlorite repairs artificial defects with a lateral diameter of 80 \( \mu \text{m} \) by local over-oxidation of PEDOT:PSS. To further demonstrate the scope of the repair procedure, as well as its compatibility with state-of-the-art OLED device manufacture, we investigated whether the same treatment also lowers the leakage current of OLED devices of which the LEP layer has not been artificially defected. In order to conclusively examine this while taking into account the sample-to-sample variation in the leakage current, a statistically relevant quantity of 43 OLED devices (ITO/PEDOT:PSS/LEP/Ba/Al) was manufactured, of which 28 were immersed for 30s in 5 wt% NaClO\textsubscript{(aq)} prior to cathode deposition, and 15 left untreated.\cite{16}

The operational characteristics of the treated and untreated devices are compared in Figure 4.5A and Figure 4.5B in which, respectively, all 43 JV- and LV- curves are assembled in the same graph. Curves corresponding to untreated devices are depicted in black and those of the treated devices are indicated in blue.

Figure 4.5A shows that the untreated OLEDs have a leakage current in the range \( 10^{-3} - 4 \times 10^{-2} \text{ mA/cm}^2 \) at \( |V| = 1 \text{ V} \), with an average of \( \sim 5 \times 10^{-3} \text{ mA/cm}^2 \). As evidenced by the blue curves, also for devices which did not undergo a deliberate maltreatment, the hypochlorite solution still effectively cancels undesired current pathways, resulting in reduction of the leakage current by about an order of magnitude down to values in the range \( 10^{-4} - 2 \times 10^{-3} \text{ mA/cm}^2 \) at \( |V| = 1 \text{ V} \), with an average of \( \sim 5 \times 10^{-4} \text{ mA/cm}^2 \). Figure 4.5B shows that the luminance of the devices is only marginally affected by the hypochlorite treatment, which is in line with the photoluminescence results (Figure 4.2A). Notably, the mere fact that a considerable improvement in performance is achieved for the treated devices demonstrates that a significant fraction of the total number of leakage paths in
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Figure 4.6: Normalized luminance plotted as function of time in hours for 25 OLED devices, of which 17 were treated with 5% NaClO\textsubscript{(aq)} for 30s (blue) and 8 were left untreated (black).

solution-processed OLEDs is indeed caused by tiny areas in which the PEDOT:PSS is more or less exposed. What’s more, it is very well thinkable that regions characterized by a locally strongly thinned LEP layer are also repaired, despite the fact that in this situation the hypochlorite can only react with the PEDOT:PSS after prior diffusion through the LEP layer. This hypothesis is supported by the observation that the untreated devices exhibit a higher number of bright spots than the treated ones, as shown by the inset photographs in Figure 4.5A. Naturally, this interpretation assumes that these bright spots are caused by an increased current density due to a locally thinned LEP layer. Upon treatment these areas are deactivated, so that small barely visible black spots remain. Finally, we note that potential uptake of water and ions by both the LEP and the PEDOT:PSS layer during the hypochlorite treatment may have long-term detrimental effects, which could limit device lifetime. Hence, the luminance of a statistically relevant set of treated devices was monitored under prolonged stress and compared with that of a set of untreated reference devices. The results are shown in Figure 4.6 which plots the luminance (blue: treated, black: untreated), normalized by its initial value \((t = 0)\), as a function of time.

The traces show that the time beyond which the luminance decreases significantly is, on average, the same for both treated and untreated devices, which shows that the repair process does not limit device life time. Close inspection of the curves tentatively leads to the conclusion that the lifetime is even somewhat longer after treatment. However, some care must be taken with this respect as the luminance of the treated devices seems to slightly increase during the first hours of operation. In summary, these experiments demonstrate that hypochlorite treatment leads to a considerable reduction in leakage current, while not limiting the operational lifetime, even for not deliberately defected OLED devices. This shows that it is of potential interest to integrate a selective oxidative treatment with pilot scale or even industrial solution-based production processes for OLEDs.
4.4 Conclusion

This chapter shows that the performance of deliberately defected, as well as intact OLED devices (glass/ITO/PEDOT:PSS/LEP/cathode), is significantly enhanced by an oxidative treatment with aqueous hypochlorite after application of the LEP layer and prior to cathode deposition. The benefit of this treatment relies on local disruption of the conductivity of the PEDOT:PSS HIL at sites where it is/has become exposed due to incomplete coverage by the LEP. This repair process was studied by creating artificial defects via local removal of LEP using laser ablation. If left untreated, device stacks containing these craters gave considerable short circuits upon cathode deposition, evidenced by a three orders of magnitude increase in leakage current and loss of diode rectification. However, treatment of the unfinished device stack with aqueous hypochlorite resulted in full "recovery" of the original low leakage current as well as diode behavior. By systematically studying the effect of immersion time and hypochlorite concentration on the PL efficiency of the LEP, suitable treatment conditions were identified guaranteeing complete disruption of PEDOT:PSS conductivity without significantly affecting luminescent properties. The repair procedure also proved successful when applied to devices which were not artificially defected, giving a further decrease in the leakage current of about an order of magnitude below the native reference level. What's more, oxidative treatment also reduced the number of bright spots induced by a locally thinned LEP layer. Device lifetimes were shown not to be affected by hypochlorite treatment, which indicates an oxidative repair step to be compatible with industrial scale OLED production.

References

3. Own work, unpublished results.
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REFERENCES


16. For this experiment blue LEP was used instead of white LEP. Visually, the luminescent properties of blue LEP had not deteriorated after 30s treatment with 5 wt.% NaClO_{aq}.
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