Redox doping in OLEDs and other organic electronics applications

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Abstract

It is well-known that PIN technology is beneficial for numerous OLED applications, e.g. active and passive matrix displays, lighting and signage. Furthermore, it can be used for other organic electronic applications such as OTFTs and organic solar cells. Here, the state of the art of the PIN technology and the latest results from the different application fields are presented.

1. Introduction

Displays based on OLED technology are not anymore a pure R&D topic. Passive Matrix (PM) OLED displays have been sold in the market for almost a decade and also the number of Active Matrix (AM) OLED displays that can be found in mobile phones and even TV sets is steadily increasing.

AM OLED displays had a difficult market entry. This was mainly related to yield issues. Both the TFT backplane and the interface between the backplane and the OLED stack caused problems. It is widely believed and even proven that a rather thick hole transport layer (HTL) may increase the yield. In order to avoid ohmic losses over the thick HTL (thick meaning well above 100 nm), the HTL should preferably be a highly conductive p-doped transport layer. Further yield increase could be observed by using a wet-processed p-doped HTL.

It is apparent to investigate the use of these so called redox doped transport layer materials (namely p- and n-doped charge carrier transport layers) also in other fields of organic and printed electronics. Both in organic thin film transistors and in organic photovoltaics the charge carrier injection and the charge carrier transport without losses is crucial. Therefore we have introduced doped transport layers in these applications. In the next sections, recent results will be presented.

2. Solution processed p-doped HTL in OLEDs

The benefits of a spin coated or printed HTL for OLEDs are mainly the substrate planarization, and the prevention of pin-holes. Furthermore, the cost for such a non-vacuum process can be lower. The standard wet-processed HTL material is PEDOT:PSS which is widely used in polymer OLEDs (PLED). However, PEDOT:PSS is an aqueous dispersion with high acidity.

Many attempts have been done to replace it with a non-aqueous, non-acidic solution. In this paper, we propose a p-doped solution of NHT-5 and NDP-9 or NDP-2 in an organic solvent. The challenge was to form a solution of neutral host, cationic host and anionic dopant species. In addition to the general advantages of a wet-processed HTL, the films processed from this solution offer a very good hole injection, a high conductivity, and high transparency. Whereas PEDOT:PSS is processed from a dispersion, the p-doped HTL is processed from a solution which eases the production.

Here we investigate Novaled's standard p-doped hole-transport system for solution processing. Thin films of NHT-5 doped with NDP-2 (named p-NHT-5 here) with about 100 nm thickness were formed by both vacuum thermal evaporation (VTE) and solution processing (spin-coating) onto glass substrates with structured ITO contacts. The concentrations of dopants in the layers were varied by co-evaporation in case of VTE and by the formulation of the solution for spin-coating. As in the case of the VTE processed layers, the conductivity of spin-coated layers can be adjusted by varying the doping concentration over several orders of magnitude. Even higher conductivities are observed for the solution processed layers, which can be interpreted by different morphology of the final layer depending on the process applied. Performance of a green OLED with spin-coated p-NHT-5 as the HTL is shown in Figure 1 with a completely VTE processed OLED as a reference. It is clearly shown that the device having spin-coated HTL is as good as the reference OLED.

One concern in solution processing is the stability of the functional solutions. It is desirable to have those solutions stable for more than tens of hours even under ambient atmosphere. Therefore, solution stability of the p-dopant has also been intensively investigated. The molecular p-dopant NDP-2 is soluble in a variety of solvents. However, not every solvent having the required solubility can be applied because solution stability, solubility of the host material, film-forming properties, and compatibility with neighboring layers needs to be considered.

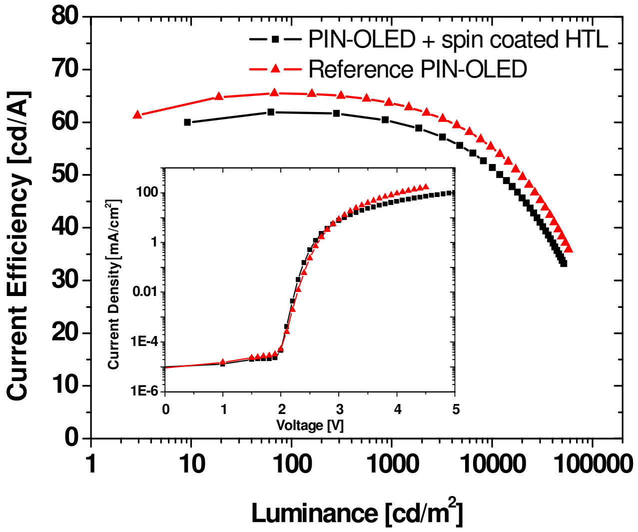

Fig. 1: LIV curves of standard PIN OLED and PIN OLED with additional solution processed p-HTL

Figure 2a shows a comparison of the stability of solutions of NHT-5 and NDP-2 towards storage in air in different solvents. Conductivity of the thin films, prepared by spin coating of the stored solutions, was measured to check the stability of the solution. It can be seen that selection of the solvent has a critical influence on the stability of a doped solution. With solvent A, the doped solution is stable for more than 3 days, keeping a high conductivity around 1E-4 S/cm.

The stability of doped thin films is even more impressive as shown in Figure 2b, where stability of conductivity of a 100 nm NHT-5 doped with NDP-9 layer is demonstrated. Conductivity at 1E-3 S/cm is kept over one month while conductivity of an intrinsic layer of NHT-5 is below 1E-8 S/cm.

3. Diffusion stability of doped transport layers

Another concern on device stability is possible diffusion and/or migration of ionized dopants during device operation. It was reported before that alkali-metal or very small molecular dopants were not fully immobile in organic layers [1]. However, this is not the case for Novaled molecular dopants since they are especially designed for high immobility, not only at room temperature but also at elevated temperatures.

We studied possible dopant diffusion/migration by determining doping profiles and interface properties with capacitance-voltage measurements (C-V) supported by impedance spectroscopy (IS). Electron-only devices containing NET-5:NDN-1 as doped electron transport layer and pure NET-5 as undoped ETL are used as the model system. The IS spectrum of such a sample can be analysed by fitting to an equivalent circuit consisting of 2 RC-units in series only:

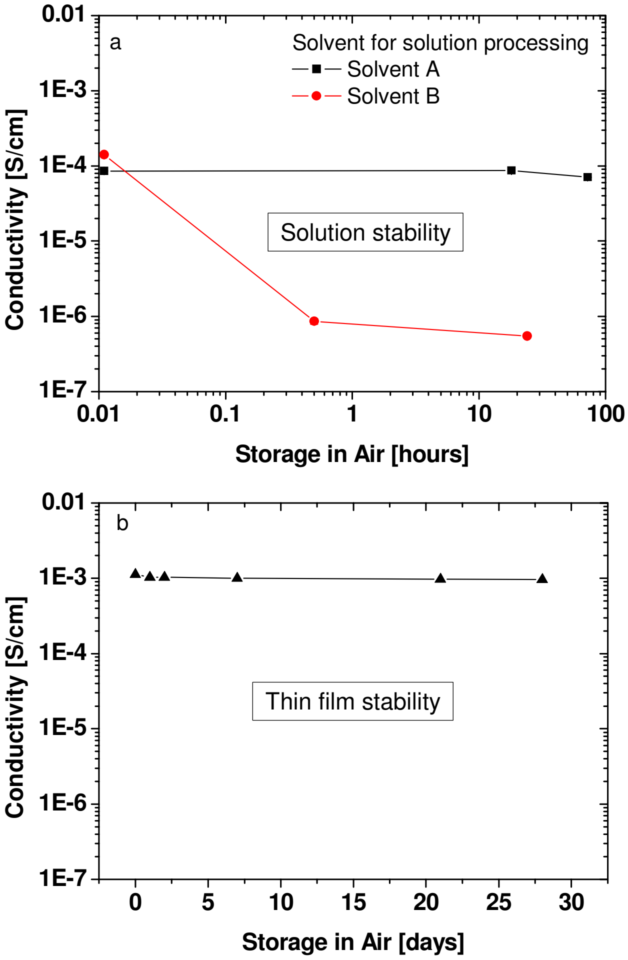

Fig. 2: a) Stability of 5 wt% solutions of NHT-5 and NDP-2. After storage of solutions in ambient atmosphere, thin films of NHT-5 doped with 1wt% of NDP-2 were spin coated, dried and conductivity was measured. b) Stability of conductivity of thin films of NHT-5 doped with 20wt% of NDP-9 when stored in ambient atmosphere

The unit having both a high resistance and high capacitance can be identified as the undoped (more specifically the low conductive) layer in the device. The other unit has a low resistance and a very low capacitance as well, which is the series resistance of the ITO electrode. No other contribution to the spectrum is observed. Further, we do not observe any component that has a medium conductivity that could result from a diffusion of dopant (NDN-1) into the undoped layer or from any interfacial layer between the doped layer and the top-electrode.

In comparison, a device with Cs as a dopant does not show an abrupt interface. The impedance spectrum exhibits an additional RC unit which has a thickness of some nanometers and exhibits a spatially inhomogeneous conductivity. We interpret this finding by Cs atoms penetrating into the underlying undoped layer, which is probably inevitable given the atomic nature and small size of the dopant.

The well defined NET-5/NDN-1:NET-5 interface allows to use the Schottky-approximation for the sample, which is a prerequisite to apply capacitance-voltage spectroscopy. As a consequence, we can use the capacitance of the low conductive layer to detect the position of the edge of the space charge layer. By monitoring how much this edge is moving with the forward bias, the density of the space charge can be calculated. This method is an extremely sensitive tool to detect potential diffusion of dopants into the undoped layer.

The distribution of donors at the interface between the doped and undoped layer is measured before stress, after applying a reverse bias of -5 V and after applying a forward bias at a current level of 10 mA/cm². It has been found that the dopants are fixed in space with a shift within only 1 nm even after stress for 1000 hours. These results clearly demonstrate that there is nearly no dopant diffusion/migration even under harsh stress.

4. Stacked PIN OLEDs

For white OLEDs, currently one of the most promising ways to make devices that combine high efficiency, long lifetime, and good color rendering index, is the so-called stacking of OLED units.

The basic layer structure of a standard non-stacked bottom-emission PIN OLED consists of a transparent anode (ITO) / p-type doped hole transport layer (HTL) / interlayer at hole side (EBL) / emission layer (e.g. matrix with phosphorescent or fluorescent emitters) / interlayer at electron side (HBL) / n-type doped electron transport layer (ETL) / metallic cathode (Al) [2].

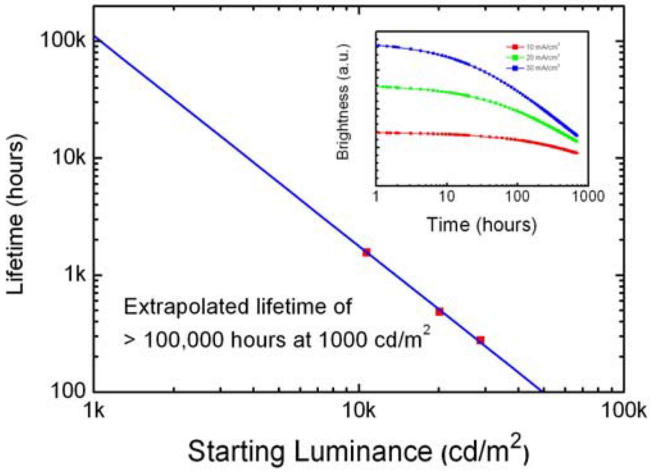

Fig. 3: Extrapolated lifetime of a stacked white OLED. Inset shows lifetime measurements at different current densities.

Since each PIN OLED starts from a highly p-type doped HTL and ends with a highly n-type doped ETL, we can just simply stack one PIN OLED on top of another PIN OLED without any intermediate layer. The p-type doped hole transport layer in previous emission unit is in contact with the n-type doped electron transport layer in the next emission unit to form a doped so called organic p-n junction. By stacking red, green and blue emission units white light can be generated [3].

Particularly, a white OLED was achieved with a power efficiency of 38 lm/W at a brightness of 1000 cd/m². The projected lifetime at this initial luminance is above 100 000 hours (see figure 3). The OLED offers an excellent CRI of 90 at color coordinates of (0.43, 0.43).

5. Use of redox doping in organic solar cells

The successful use of redox dopants in connecting units of stacked OLEDs has been proven several times. The approach of stacking is also investigated for organic solar cells (OSC) in order to achieve an optimum harvesting of the complete sun spectrum. This can be achieved by stacking two organic solar cell units on top of each other, whose photoactive layers absorb in different regions of the visible light, e.g. red and green. The requirements for the p-dopant in OPV are even harder as compared to PIN-OLEDs. A particularly strong acceptor material is needed to allow for a high efficiency: Due to the use of a very strong acceptor material as p-dopant, HTLs with very deep HOMO can be used. This allows for better energy alignment between the absorber and the HTL and this increases the fill factor of the solar cell. Experiments that were done at Heliatek GmbH showed a relative increase of the fill factor of an organic solar cells of 35% when the p-dopant NDP-2 was replaced by the stronger dopant NDP-9 (see figure 4).

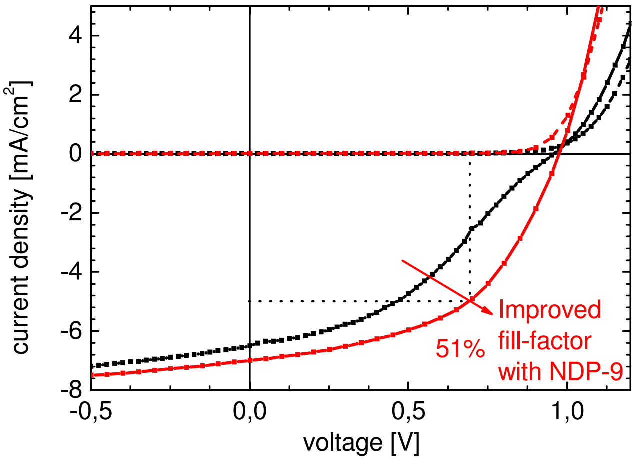

Fig. 4: Current density vs. Voltage of organic solar cell containing NDP-2 (black curve) and NDP-9 (red curve)

By using Novaled redox dopants, tandem solar cells with a high open circuit voltage (1.9V), high fill factor (60%) and high lifetime (light dose of three years at 50°C with hardly any degradation) could be demonstrated by Heliatek [4].

6. Use of redox doping in organic TFTs

As already demonstrated above, Novaled molecular dopants can be rather easily solution processed while still remain good function. Therefore, redox doping can also find application in a much wider field of organic electronics where solution process is preferred due to its potentially low cost. In addition, it has also been shown that there is nearly no dopant diffusion/migration in organic layers with Novaled molecular dopants even under high electrical field during device operation. Consequently, redox doping may become relevant for organic thin-film transistors (OTFTs) where the carrier injection from drain and source into the organic material has a major influence on the device performance. Here we show how interface problems between electrode and semiconductor can be largely diminished by injection layers based on strong molecular dopants. Table 1 shows results of OTFTs using Al as source/drain (S/D) electrodes and an ambipolar organic semiconductor. Without any injection layer (IL) in between the S/D and the semiconductor layer, the OTFTs show expected ambipolar properties but with extremely low hole and electron mobilities. By insertion of Novaled p-dopant NDP-9 in between S/D and the semiconductor, the OTFT is completely transformed into an unipolar p-type device with hole mobility improvement by a factor of 70, which indicates greatly enhanced hole injection as well as complete suppression of electron injection when driving at n-type mode. In contrast, the OTFT show absolutely n-type behaviour with electron mobility improvement by more than 3 orders of magnitude by insertion of Novaled n-dopant NDN-1. It is clearly demonstrated that it is possible to modify and define the polarity of a TFT device by simply using Novaled doped or dopant injection layer. Hence, Novaled molecular dopants make it possible to use only one kind of semiconductor to fabricate organic inverter or even CMOS [5].

Injection layer	Conduction type	Mobility μ [cm^2/Vs]		Mobility improvement by IL	
-	ambipolar	(p) 1.5E-4	(n) 1.0E-5	-	-
NDP-9	p type	(p) 0.01	-	× 70	-
NDN-1	n type	-	(n) 0.025	-	× 2500

Table 1: Summary of OTFT performance with and without injection layers based on both p- and n-type molecular dopants

7. Summary

So-called redox doped hole and electron transport layers reduce the resistivity of the organic material by several orders of magnitude and allow for barrier-free charge carrier injection from the electrodes into the organic stack. Therefore they can be successfully implemented in all kinds of organic electronic applications in which charge carrier injection and transport is important such as standard OLEDs, inverted OLEDs, stacked OLEDs, top-emitting OLEDs, OTFTs and in OPV.

8. References

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