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Enhancing the electron injection in polymer light-emitting diodes using a sodium stearate/aluminum bilayer cathode

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ABSTRACT

In this contribution the molecule sodium stearate (NaSt) is used for the first time as electron injection layer in combination with the fluorescent polymer phenylene substituted poly (para-phenylenevinylene) (Ph-PPV) in organic light-emitting diodes (OLEDs). The fabricated devices show current efficiencies up to 8.4 cd/A, indicating that the employed NaSt/aluminum (Al) bilayer cathode has adequate electron injection capabilities in conjunction with Ph-PPV and, therefore, NaSt has the potential to become a non-toxic alternative to the widely-used alkali halide lithium fluoride (LiF).

Numerical simulations of the device structure are performed which are in good agreement with the experiments. Additionally, it is shown that the NaSt/Al cathode of the presented device cannot be simply modeled by using a low work function contact, as it is commonly done for the LiF/Al cathode in simulations of multilayer devices. Instead, an alternative approach is introduced in which an insulator in combination with the Fowler–Nordheim tunneling and the direct tunneling model is chosen to describe the charge carrier injection through the NaSt layer.

1. Introduction

Since Tang and Van Slyke [1] demonstrated their first low operation voltage driven organic light-emitting diode (OLED) in 1987, OLEDs have been extensively researched and greatly improved in the last decades. Nowadays, OLEDs are already commercially utilized in electronic display applications, and in the near future, OLED lightings are believed to lead to a paradigm shift in the lighting industry [2]. Despite this rapid evolution, there is still much room for further research and optimization, especially regarding lifetime, production costs, efficiency and environmental safety.

Since the OLED operation principle is essentially based on pair-wise recombination of electrons and holes, followed by the formation and radiative decay of excited states in the light-emitting layer, the OLEDs efficiency proportionately depends on the charge carrier balance factor (which is the ratio of electrons to holes at the recombination region). Thus, it is a crucial task during OLED device design, to optimize the charge carrier balance, which is mainly determined by two physical parameters: injection barrier height and charge carrier mobility [3].

In order to achieve a low injection barrier height for holes, the work function of the anode has to match the highest occupied molecular orbital (HOMO) of the organic semiconductor. Therefore, materials with high work functions (e.g. noble metals like Au) are required. The most common anode material, however, is indium tin oxide (ITO) [4] due to its high transparency and conductivity. The injection property of the ITO anode is usually improved by a hole-injection layer (HIL), consisting of the conductive, transparent and high work function polymer mixture poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) [5,6].

In order to attain an effective electron injection into the lowest unoccupied molecular orbital (LUMO) of the semiconductor, low work function metals such as Li, Ca, Ba and Mg are necessary. These base metals, however, are

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utmost vulnerable to moisture and oxygen [7] and can also chemically react with the organic material [4]. The search for more stable cathode materials with good electron injection properties has lead to bilayer cathodes, consisting of an ultrathin insulating buffer layer (e.g. LiF [8], CsF [9]), Al_2O_3 [10] or MgO [11]), capped with an air-stable metal like Al or Ag. Nowadays, the LiF/Al bilayer cathode is the state of the art [12].

In this work, we utilize the amphiphilic molecule sodium stearate (NaSt, $C_{17}H_{35}COONa$) as an alternative buffer layer material for polymer light-emitting diodes (PLEDs), based on the high-efficiency fluorescent light-emitter phenylene substituted poly (para-phenylenevinylene) (Ph-PPV), also known as 'Super-Yellow' (SY). So far, NaSt has solely been investigated in small molecule OLEDs (SMOLEDs), based on Aluminum-tris (8-hydroxychinolin) (Alq_3) [13–15] or naphthalimide derivatives [16], but, to our knowledge, no studies on the effects of a NaSt buffer layer on the performance of PLEDs have been accomplished. In a direct comparison between SMOLEDs which were fabricated with either NaSt or LiF as cathode buffer layer, the usage of NaSt resulted in similar luminance but with a superior thermal stability [13]. However, these results cannot be simply adopted to Ph-PPV-based PLEDs, because the injection capability of electrons from the cathode to the organic layer depends on parameters like the energy difference between the conduction band minimum of the buffer layer and the LUMO of the organic layer, as well as the thickness and the resistivity of both layers [17,18].

The promising facts described above were the motivation for this present work, in which we investigate the impact of an ultrathin NaSt buffer layer on the performance of Ph-PPV-based OLEDs. In Section 2 of this report, we explain the fabrication and characterization of our devices and show the results of the measurements performed on these devices. Section 3 focuses on the device simulation of the OLED structure. The used mathematical models and material parameters are presented and the simulation results are compared with experimental data. In Section 4, a short summary of the paper is given.

2. Experimental

2.1. Device fabrication

The OLEDs investigated in this work have the layer structure ITO/ PEDOT:PSS (40 nm)/ SY (80 nm)/ NaSt (x nm)/ Al (200 nm), where the thickness x of the NaSt layer was varied between 0 nm and 4 nm. A schematic energy level diagram of that structure is shown in Fig. 1.

Glass substrates coated with ITO (sheet resistance 10 Ω/□) were first ultrasonically cleaned, then cleaned with acetone and isopropyl alcohol, dried under a nitrogen flow and, lastly, treated with ozone (10 min). Afterwards, a 40 nm thin HIL, consisting of PEDOT:PSS (Clevios-P Al 4083, purchased from Heraeus Clevios GmbH), was deposited on the ITO glasses by spin coating. The substrates were then baked for 15 min at 130 °C in a nitrogen-filled glovebox (<1 ppm H_2O/O_2). Super-Yellow (PDY-132, purchased

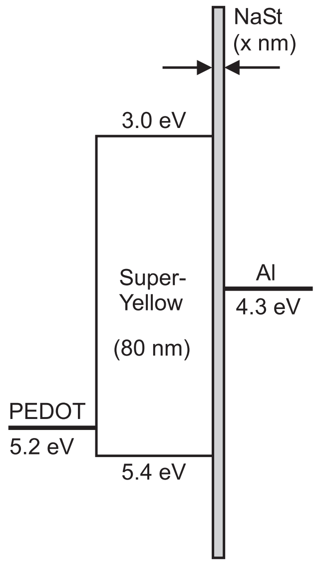

Fig. 1. Schematic energy level diagram of the ITO/PEDOT:PSS/SY/NaSt/Al – device.

from Merck KGaA), dissolved in toluene (4,5 mg/ml), was then spin-casted (80 nm) and baked for 1 h at 110 °C in a nitrogen environment. The layer thickness was afterwards controlled using a Veeco Dektak 150 surface profilometer. The NaSt (purchased from Sigma–Aldrich) buffer layer and the Al cathodes were fabricated by vacuum deposition at a base pressure of 2×10^{-6} mbar. A shadow mask was used to produce an OLED array, consisting of 8×8 units, each one 3 mm $\times$ 3 mm in size. NaSt was deposited at a growth rate of approximately 0.5 nm/min, whereas the variation of the buffer layer thickness from 0 nm to 4 nm in 0.5 nm steps was achieved by a stepwise moving shutter. We note that the NaSt layer thickness was calibrated using AFM (atomic force microscopy) reference measurements prior to the device fabrication. The current–voltage characteristics were obtained using an Agilent 4156 C Precision Semiconductor Parameter Analyzer. Luminance was measured using a Konica Minolta LS-110 Luminance Meter. All measurements were carried out in a nitrogen environment.

2.2. Measurement results

The first series of experiments was performed in order to determine the optimum thickness of the NaSt buffer layer in terms of maximum current efficiency. Thus, at a constant current density of 100 mA/cm^2, the luminance of OLEDs with various NaSt layer thicknesses was measured. As can be seen from the measurement results shown in the inset of Fig. 2, the optimum buffer layer thickness is 2 nm, which leads to a luminance of 8000 cd/m^2 and a current efficiency of 8 cd/A.

In the second series of experiments, OLEDs with optimized buffer layer thickness (2 nm NaSt) were compared to reference devices without buffer layer (0 nm NaSt). The resulting luminance–voltage (L–V) characteristics shown in Fig. 2 clearly indicate, that the application of