Organic Electronics 49 (2017) 24–32

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Inkjet deposition of a hole-transporting small molecule to realize a hybrid solution-evaporation green top-emitting OLED

S. Olivier [a, b], E. Ishow [b], S. Meunier Della-Gatta [a], T. Maindron [a, *]

[a] Université Grenoble-Alpes, CEA, Leti, MINATEC Campus, 17 rue des Martyrs, F-38054, Grenoble Cedex 9, France
[b] CEISAM - CNRS UMR 6230, Université de Nantes, 2 rue de la Houssinière, F-44322, Nantes, France

ARTICLE INFO

Article history:
Received 7 March 2017
Received in revised form
5 May 2017
Accepted 9 June 2017
Available online 15 June 2017

Keywords:
OLED
Solution-deposition technique
Inkjet printing thin-film encapsulation

ABSTRACT

The QUPD molecule has been deposited by inkjet printing as a hole-transport layer in top-emitting green OLEDs. A systematic study of the QUPD-based ink formulation has been done and different solvent mixtures have been investigated, in order to find the best composition (QUPD in toluene/IPA/anisole, 8/1/1 v/v/v) leading to the best film forming properties. Spin-coated PEDOT-PSS has been used as hole injecting layer. Subsequent layers have been deposited by vacuum sublimation. The resulting hybrid, solution-sublimation, OLEDs have been encapsulated by atomic layer deposition using Al_2O_3 material. In order to overcome the issue related to the thickness control of the organic layers deposited from solution, second order cavity length OLEDs have been fabricated by modifying the n-doped electron transport layer thickness. In that case, the relative OLED efficiency variation (10.5%) due to the thickness variation is far less compared to first order cavity length (34%) allowing a better reproducibility of the OLED fabrication. In the end, high efficiency (18 lm/W) green OLEDs of two different sizes, 0.44 cm^2 and 4 cm^2, have been fabricated, using an inkjet printed QUPD layer as hole transporting layer.

1. Introduction

Since the discovery of conjugated polymers in the 1970s [1,2], the research field in organic electronics has been widely studied because of numerous potentials offered by the use of organic semi-conductors in organic solar photovoltaic cells (OPVs), organic light-emitting diodes (OLEDs) or organic thin-film transistors (OTFTs). In particular, the use of soluble organic semi-conductors, conjugated polymers as well as small molecules, allows the fabrication of these organic circuits out from solution, through cheaper and less energy-consuming processes than standard ones used with inorganic semi-conductors [3–5]. The inkjet-printing technology turns out to be an interesting candidate for solution-processing of organic semi-conductors because it is an additive manufacturing technology that allows their selective deposition onto a predefined pattern, as for instance OLED pixels in a display. It also benefits from straightforward scale-up and low fabrication costs thanks to efficient material usage compared to other printing techniques or vacuum evaporation [6,7]. Today, in the world of OLEDs, large efforts are being pushed towards the development of inkjet-printed small molecules [8] to fabricate the next generation of flat panel displays [3].

Organic electronic devices require generally amorphous and flat film topography with a film thickness of only a few tens of nanometers, onto a dedicated substrate with a dedicated electrode material (metal or transparent conductive oxide like the well-known ITO) whose surface properties can differ much from those of a paper sheet for which inkjet printing technology has been developed originally. The film properties specifications are quite high and cannot be obtained using inkjet printing without optimization of the deposition parameters like the ink composition, viscosity, rheology or surface energy of the substrate, for one given material [4,9–11]. Besides, in order to deposit a given solution comprising an organic semiconductor onto a given pattern, for instance a dedicated pixel area in a display, a bank structure is usually applied around the said given pixel area [12].

Historically, the inkjet printing has been mainly applied to the deposition of π–conjugated polymer solutions to make displays and only few examples of publications describe the inkjet-printing of organic small molecule materials for making organic devices [7,13–19]. Among these examples, a few of them describe the realization of OLED architectures containing at least one inkjet-printed layers [7,13,16,18,19] and, to the best of our knowledge,

* Corresponding author.
E-mail address: tony.maindron@cea.fr (T. Maindron).

http://dx.doi.org/10.1016/j.orgel.2017.06.017
1566-1199/

only one describes the realization of a top-emitting OLED structure containing at least one inkjet-printed layer [20]. In top-emitting OLED architectures, where the light is extracted out opposite to the substrate, through a semi-transparent electrode, organic layer thicknesses must be precisely controlled in the OLED architecture in order to define the right optical cavity length corresponding to a given emission wavelength inside the cavity (Fabry-Perot resonator) [21]. Making vapour-deposited top-emitting OLED structures is not an issue because high precision quartz crystal microbalances (QCM) can be used to monitor the organic material evaporation with angstrom-scale accuracy. However, for solution processes including the inkjet printing technology, the thickness control is not as accurate as with QCMs, resulting in an optical cavity length that could not be well tuned to the emission colour of the emitter inside the cavity, resulting in a colour-shift as well as in a decreased OLED efficiency.

This work reports the study and realization of ink-jet printed films of the QUPD (N4,N4′-Bis (4-(6-((3-ethyloxetan-3-yl)methoxy) hexyloxy)phenyl)-N4,N4'-bis(4-methoxyphenyl)biphenyl-4,4'-diamine) molecule, with a full insight into an optimization procedure of the ink formulation. In a second time, the QUPD films, used as Hole-Transporting Layer (HTL), will be incorporated into a hybrid solution/vacuum evaporation top-emitting green OLED. The choice for this molecule has been motivated by its photopolymerizable nature [22] which should theoretically enable easy subsequent deposition of an emitting layer on the top (not investigated in this work). OLED encapsulation using a single ALD-deposited Al_2O_3 thin film has been performed in order to avoid alteration of the device by ambient air.

2. Experiment

Preliminary printing tests have been realized onto 100 mm silicon wafers covered with 40 nm-thick spun-cast layer of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS) type Clevios™ Al4083 from Heraeus, subsequently baked at 120 °C during 20 min. The printed HTL material was QUPD purchased from Lumtec and doped with 4% mol. of the photoinitiator 4-octyloxydiphenyliodonium hexafluoroantimonate (OPPI) purchased from Spectra Group Limited. All Solvents used in the ink formulations (toluene, iso-propanol (IPA), dimethyl sulfoxide (DMSO) and anisole) were purchased from Aldrich. All the formulations have been filtered with a PTFE filter (Millex®, 0.45 μm) before filling on a clean cartridge of the printer. Inkjet depositions were performed with a Fujifilm Dimatix DMP-2831 using a DMP-11610 printhead composed of 16 nozzles with a pitch of 254 μm and a drop volume of approximately 10 pl.

OLED devices were fabricated onto 200 mm silicon substrates with Al:Cu 1%/TiN (7 nm) as a bottom reflective anode. The device pattern was such that 135 OLED (9×5 mm^2) devices could be made at the same time onto the whole wafer. Insulating positive resists were used in order to define the active zone where the organic layers had to be deposited as well as to ensure electrical insulation between the bottom anode and the vacuum-deposited cathode. The whole process took place in a clean room environment.

The wafers were prepared by an Ar-plasma surface treatment (60 W, 60 s). The first layer in PEDOT-PSS (40 nm) type Clevios™ Al4083 was deposited by spin-coating and then baked during 20 min on a hotplate at 120 °C in ambient air. Then, the organic layer was exposed to UV ozone treatment during 6 min in order to facilitate the inkjet printing process of the subsequent QUPD layer onto PEDOT-PSS as well as to increase its electrical conductivity as described in Ref. [23].

For device **A** (Fig. 1), all layers on top of PEDOT-PSS have been deposited in sequence by vacuum evaporation using a SPECTROS© 200 from Kurt J. Lesker company. The NPB (N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine) molecule was purchased from Sensient, TCTA (tris(4-carbazoyl-9-ylphenyl)amine) and Ir(mppy)$_3$ (tris[2-(p -tolyl)pyridine]iridium(III)) molecules from Lumtec company. The Hole-Blocking Layer (HBL, 5 nm) and the n-doped Electron-Transport Layer (ETL, 120 nm) could not be disclosed in this work due to a collaborative agreement policy. However, because the paper mainly focuses onto the inkjet printing of QUPD, we think that these missing data are not impacting much the quality of the work and that any other scientists may use any other HBL and ETL solutions with success. The top semi-transparent cathode is made of a Ca/Ag (7 nm/10 nm) bilayer which use has been motivated by the former work from Pode et al. who demonstrated that a suitable combination of thicknesses of these two materials can give rise to a higher transmission in the visible than that provided by individual metal layers with equivalent thicknesses [24]. In our case, this option was useful to increase the transmission of the top electrode so as to reduce as much as possible the interference pattern inside the Fabry-Perot cavity. The thick ETL was used in order to tune the optical cavity to the second optical order. Therefore, the n-doping of the ETL allowed us to

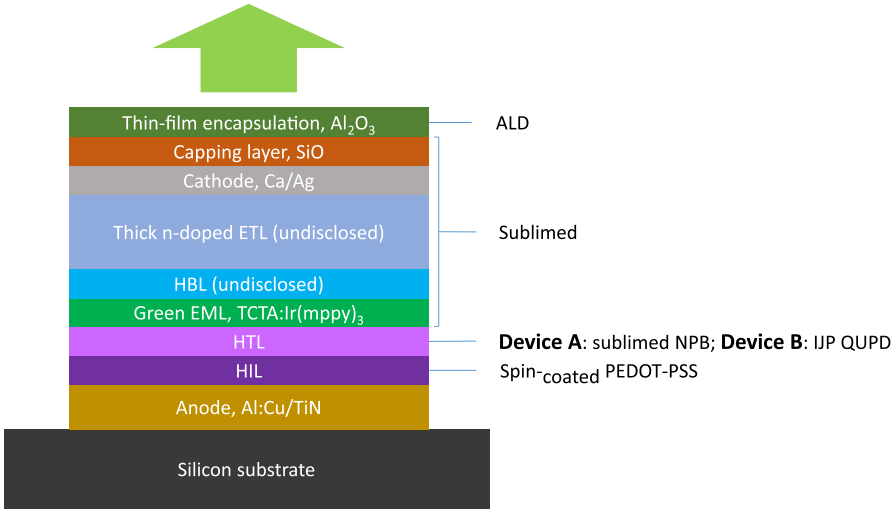

Fig. 1. Structures of the second order cavity OLED devices (120 nm thick ETL, not at scale) incorporating one (device **A**) and two (device **B**) layers made from solution.