Blade Coating System for Organic Electronics

Viviane N. Hamanaka^{1,2}, Remco J. van Dasselaar³, Marcos H. M. O. Hamanaka⁴, Natanael L. Dias⁴, Vinicius L. Pimentel⁴, Maria Cecilia Q. Bazetto⁴, Hany Aziz², Fernando J. Fonseca¹

¹Escola Politécnica da Universidade de São Paulo, Departamento de Engenharia de Sistemas Eletrônicos, São Paulo, SP, Brazil. ²Department of Electrical and Computer Engineering, University of Waterloo, Waterloo, Ontario, Canada.³Department of Mechanics of Solids, Surfaces & Systems, Faculty of Engineering Technology, University of Twente, The Netherlands.

⁴Centro de Tecnologia da Informação Renato Archer, Campinas, SP, Brazil.

e-mail: vnhamanaka@usp.br

Abstract— In this work we show the project and fabrication of a home-made blade coating system for deposition of solutions of organic semiconductor materials. The system was used for deposition of PEDOT:PSS, a common hole injection material in solution based organic light emitting diodes (OLEDs). Phosphorescent OLEDs were assembled with PEDOT:PSS deposited by blade coating and also by spin coating for comparison. Both devices presented similar performance with low leakage current and driving voltages around 6 V (at 20 mA/cm²). The efficiency for both devices was very similar (EQE ~ 17%, at 20 mA/cm²) showing that the PEDOT:PSS film obtained by blade coating has similar hole injection properties and performance as the film deposited by spin coating.

Keywords—Organic electronics, blade coating, OLED, solution coating

I. INTRODUCTION

Organic electronic devices are actively being pursued for flexible, transparent, large-area, and low-cost applications [1-4]. To fully explore the potential of these devices it is desirable to have solution coating processes to deposit the organic semiconductor materials. Spin coating is the most ubiquitous solution-coating method in the literature to date [5]. While the technique is useful for experimental work, it is difficult to scale up for high-volume manufacturing and is not suitable for large-area device fabrication. Blade coating, in contrast, is a simple, scalable, cost-effective, and roll-to-roll compatible process for the fabrication of organic electronic based devices [1-4]. In addition, blade coating minimizes wasted material, is compatible with a variety of different substrates and provides excellent film uniformity over large areas [2, 4]. Fig. 1 illustrates the blade coating process in which the substrate is placed on a hotplate and the organic material solution is placed on the substrate in front of the blade. The blade is then moved forming a thin film. For deposition of multilayers of organic materials and large area deposition it is important to have two heating sources to achieve high uniformity and to avoid dissolution of the bottom layer by the solvent of the next layer [4].



Fig. 1. Illustration of the blade coating process for deposition of organic materials.

II. METHODOLOGY

Fig. 2 shows a drawing of the mechanical design for the automated blade coating system with its four main parts: (a) spindle cart system to move the blade over the substrate, (b) blade, (c) hot plate and (d) infrared lamp.



Fig. 2. Drawing of the automated blade coating system with the main parts.

This system was used to deposit PEDOT:PSS thin films. PEDOT:PSS (Sigma Aldrich, 2.8 wt % dispersion in H₂O, low conductivity grade) solutions were prepared by diluting with 2-propanol in a 1:5 (spin coating) and 1:3 (blade coating) volume ratio and filtering with a 0.45 µm PVDF filter. The solutions were deposited on ITO patterned glass substrates (substrate size: 2.54 x 2.54 cm, sheet resistance: 20 Ω/sq , Kintec) by spin coating (5000 rpm for 60s) and blade coating (blade gap = 100 μ m, volume = 13 μ L, speed = 20 mm/s, hotplate temperature = 80 °C) and annealed at 130 °C for 1 hour under ambient conditions. For spin coating deposition, glass-ITO substrates were submitted to RIE O₂ plasma treatment prior to the PEDOT:PSS deposition. OLED devices with an active area of 0.04 cm^2 and following structure were made: glass-ITO/PEDOT:PSS (25 nm)/CBP (30)nm)/CBP:Ir(ppy)3 (5%, 15 nm)/TPBi (40 nm)/LiF (1 nm)/A1 (80 nm). PEDOT:PSS, CBP and Ir(ppy)₃ function as the hole injection layer (HIL), hole transport layer (HTL), and phosphorescent guest dopant, respectively. TPBi (2,2,2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) is used as the electron transport layer (ETL) and LiF is the electron injection layer. Indium tin oxide (ITO) and Al are used as the anode and cathode contacts respectively. Except PEDOT:PSS, all other layers were coated by vacuum thermal evaporation using an Angstrom Engineering EvoVac system at deposition rates of 0.1-2 Å/s (base pressure $< 5 \times 10^{-6}$ Torr). Current-voltage-luminance measurements were carried out using an Agilent 4155C Semiconductor Parameter Analyzer connected to a silicon photodiode. All electroluminescence (EL) lifetime tests were carried out at a current density of 20 mA/cm² using a custom-built lifetime test setup. The devices were kept in a N_2 atmosphere at all times. Morphology and roughness analysis of PEDOT:PSS films were obtained by atomic force microscopy (AFM) (NanoSurf EasyScan 2). Thickness measurements were performed using a contact profilometer DektakXT (Bruker).

III. RESULTS

A. Automated Blade Coating System

Fig. 3 shows a photo of the blade coating system with the main parts: a) Motor: A 24V permanent magnet servo motor (Electro-Craft Corporation) is used to direct drive the spindle. It is supplied with 12V and 2A using the L298N h-bridge driver. b) Deposition control: an Arduino DUE is used to control the setup. Its processor runs on 16 kHz. Control of the speed is done using PID feed-back and feed-forward by an Arduino DUE with a clear interface to the user, with options to adjust the desired blade speed in a range of 5 to 100 mm/s. Two switches (MarGerius 40000) are mounted below the hot plate for safety and calibration reasons. c) Hot plate and temperature control: a silicone rubber heater (Watlow) with temperature up to 260 °C was attached to the back of a 1 cm thick aluminum plate. The temperature of the hotplate is actively controlled by an external PID (West P6100). The aluminum plate presents a central hole that accommodates a type K thermocouple that is connected to the external PID. d) An Infrared (IR) lamp (250 W) is used as a top heating source in order to provide fast solvent removal from the coated films. The distance between the lamp and the aluminum plate can be adjusted. A servo motor (MG90S) is used to open and close the shutter of the IR lamp. Because of the heat, a servo with steel internal gears is used. e) The blade presents two micrometers to set the distance between the blade and the substrate. The maximum deposition area is 120 mm (width) x 250 mm (length).



Fig. 3. Photo of the automated blade coating system with the main parts.

B. Develompment of OLEDs

PEDOT:PSS is the most common hole injection and extraction layers in solution coated organic optoelectronic devices such as organic light emitting diodes (OLEDs) and organic solar cells (OSCs) [4, 6]. Fig. 4 shows the atomic force microscopy (AFM) images of PEDOT:PSS films deposited by spin coating and blade coating. The root-meansquare roughness (Rms) was 1.14 ± 0.06 nm and 2.02 ± 0.13 nm for the spin-coated and blade-coated films, respectively. The higher roughness value of the blade coated film may be attributed to the relatively faster evaporation rate of 2-propanol (used to dilute the PEDOT:PSS solution and achieve the desired film thickness). During the film coating, the hotplate temperature is set to 80 °C; the boiling point of 2-propanol is 82.5 °C. Therefore, the solvent evaporates significantly faster compared to the spin-coated films, facilitating void formation and resulting in a less smooth film. The average thickness of the films was 24.1 ± 4.6 nm (blade coating) and 24.5 ± 1.3 nm (spin coating) (average thickness of 9 points for each sample, for a minimum of 3 samples).



Fig. 4 Atomic Force Microscopy (AFM) images of PEDOT:PSS films deposited on glass-ITO substrates by spin coating (a) and blade coating (b). Area = $10 \times 10 \mu m$.

To investigate how the hole injection properties of PEDOT:PSS were affected by the different solution coating methods, OLED devices were made with the following structure: glass-ITO/PEDOT:PSS (25 nm)/CBP (30 nm)/CBP:Ir(ppy)₃ (5 %, 15 nm)/TPBi (40 nm)/LiF (1 nm)/A1 (80 nm), where PEDOT:PSS was deposited by spin coating or blade coating and all other layers were thermally evaporated. Fig 5 shows the current density versus voltage curves and Fig 6 shows the external quantum efficiency (EQE) versus current density for the devices. From Fig 5 (a) it can be clearly seen that both devices present similar performance with low leakage current and driving voltages around 6 V (at 20 mA/cm²). Fig 5 (b) shows that both devices present EQEs of approximately 17% (at 20 mA/cm²).



Fig. 5. Current density versus voltage (I-V) curves for OLEDs with PEDOT:PSS deposited by blade coating (red line) and spin coating (black line).



Fig. 6. EQE versus current density curves for OLEDs with PEDOT:PSS deposited by blade coating (red line) and spin coating (black line).

Fig. 7. presents lifetime characteristics representing relative changes in luminance and driving voltage over time under constant current driving of 20 mA/cm² for OLEDs with HIL deposited by different methods. For the stability traces, normalized luminance is plotted on the primary y-axis and the change in driving voltage (ΔV) with respect to the initial (time zero) driving voltage is plotted on the secondary y-axis. Regardless the deposition method for the HIL, both devices presented luminescence half-life (LT50, defined as the time elapsed until the luminance decreases to half its initial value under constant current driving) in the range of 30 minutes. The EL lifetimes of the devices are consistent with recent results, showing that electron leakage to the PEDOT:PSS HIL plays a considerable role in limiting EL lifetime [7]. The remarkably similar performance and stability of the devices with the HIL deposited by spin coating and blade coating shows that despite the differences in surface roughness and thickness distribution observed previously, there was no effect on the hole injection properties of PEDOT:PSS.



Fig. 7. Lifetime characteristics (relative changes in luminance and driving voltage versus time) of OLEDs with PEDOT:PSS deposited by blade coating (red line) and spin coating (black line).

CONCLUSIONS

Blade Coating was successfully used to obtain very thin and uniform PEDOT:PSS films with low roughness that were used as HIL in phosphorescent OLEDs. This method does not require the previous treatment of the ITO by RIE O_2 plasma and presents very low material waste. The results presented shows that the blade coating system assembled is suitable for the deposition of very thin and uniform films of organic materials not only for OLEDs but other organic semiconductor solution-based devices such as organic solar cells and organic sensors.

ACKNOWLEDGMENT

V. N. H. thanks CNPq and Capes for financial support (grants numbers: 141986/2015-8 and PDSE 88881.187025/2018-01, respectively).

References

- D. Han, Y. Khan, J. Ting, S. M. King, N. Yaacobi-Gross, M. J. Humphries, C. J. Newsome, A. C. Arias, "Flexible Blade-Coated Multicolor Polymer Light-Emitting Diodes for Optoelectronic Sensors", *Adv. Mater.* 29 (2017) 1606206.
- [2] P-T. Tsai, K-C. Yu, C-J. Chang, S-F. Horng, H-F. Meng, "Large-area organic solar cells by accelerated blade coating", *Organic Electronics* 22 (2015) 166.
- [3] Q. Zeng, Z. Xu, C. Zheng, Y. Liu, W. Chen, T. Guo, F. Li, C. Xiang, Y. Yang, W. Cao, X. Xie, X. Yan, L. Qian, P. H. Holloway, "Improving Charge Injection via a Blade-Coating Molybdenum Oxide Layer: Toward High-Performance Large-Area Quantum-Dot Light-Emitting Diodes" ACS Appl. Mater. Interfaces 10 (2018) 8258.
- [4] C-Y. Chen, H-W. Chang, Y-F. Chang, B-J. Chang, Y-S. Lin, "Continuous blade coating for multi-layer large-area organic light emitting diode and solar cell", *J. Appl. Phys.* **110** (2011) 094501.
- [5] S. R. Forrest, The path to ubiquitous and low-cost organic electronic appliances on plastic, Nature 428 (2004) 911–918.
- [6] Stephan Kirchmeyer and Knud Reuter, "Scientific importance, properties and growing applications of poly(3,4ethylenedioxythiophene)," J. Mater. Chem., vol. 15, pp. 2077–2088, 2005.
- [7] E. Salsberg, H. Aziz, "Degradation of PEDOT:PSS hole injection layers by electrons in organic light emitting devices", Organic Electronics 69 (2019) 313.