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Patterning quality control of inkjet printed PEDOT:PSS films by wetting properties

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ABSTRACT

In this contribution, we describe the development of inkjet printable PEDOT:PSS polymer-based inks for fabrication of polymeric organic light-emitting devices (OLEDs). By using a 10 × 10 array of SU8 wells on ITO/glass substrates, guided deposition of PEDOT in a simulated OLED pixel structure was possible. The quality of the printed patterns was controlled by fine tuning of the surface wetting properties using self-assembled monolayers (SAMs) and/or oxygen reactive plasma. All the investigated surface treatments improved the quality of the printed pattern. However, the O_2 plasma treated surfaces, which had the highest free energy, resulted in smoother and more uniform PEDOT films than did the SAM-coated surfaces. Rainbow-like features and non-uniformities observed at the edges of the film were attributed mostly to the well-known coffee stain effect and the drying environment. A good reduction of such features was achieved by decreasing the PEDOT content in the inks.

1. Introduction

One of the driving forces for flexible electronics is the promise of low-cost production with high yield and throughput using roll-to-roll (R2R) processes. Deposition methods based on solution-processable materials such as ink-jetting, screen and flexo/gravure printing, and spray coating are more easily adapted to an R2R environment compared to vacuum-based ones [1,2]. One of the most straightforward approaches towards achieving locally patterned functional materials involves depositing them directly in a pattern using inkjet printing (IJP) [3–7]. For most applications in electronic devices, the drop-on-demand (DOD) jetting mode is the best choice due to its smaller drop size and higher placement accuracy. The feature size and the quality of the printed pattern are ultimately determined by drop volume and the interaction of the jetting fluid with the substrate. Fig. 1 illustrates the influence of the substrate on drop spread. Dot gain is calculated as the ratio in diameter of the spread drop (d_c) and drop diameter (d_a). The smallest printed feature would have a width equal to the diameter of the drop. Drop spread is influenced by fluid properties such as surface tension and viscosity plus the relative surface energy and roughness of the substrate. So it is possible to limit drop spread by carefully modifying the surface energy of the substrate and/or confining the fluid by creating cavities or wells on the substrate [8,9]. The last is the approach usually taken to define pixels in polymeric OLED displays and in color filters for LCDs.

In this contribution, we describe the development of inkjet printable PEDOT:PSS polymer-based inks for fabrication of polymeric OLED devices. PEDOT:PSS is a well known, studied and widely employed thiophene derivative polymer, that has been used as hole injection layer in OLEDs [10–12]. The quality of the printed patterns was controlled by fine tuning the surface wetting properties using self-assembled monolayers (SAMs) and/or oxygen reactive plasma. The role of the surface treatment on the chemical and physical properties of ITO and SU-8 photoresist films was evaluated by contact angle and surface energy measurements, atomic force microscopy (AFM), optical profilometry and microscopy.

2. Experimental

2.1. General

PEDOT:PSS (Clevios P VP AL4083, 1.3–1.7% solid content) from H.C. Starck was used as received in the preparation of inkjet inks 1–3. Other chemicals were acquired from Sigma–Aldrich Co. and used without further purification. ITO coated glass substrates (R_S = 10–12 Ω/□, PGO-Praezisions Glass & Optik GmbH) were cleaned in a class 10.000 clean room using a sequence of

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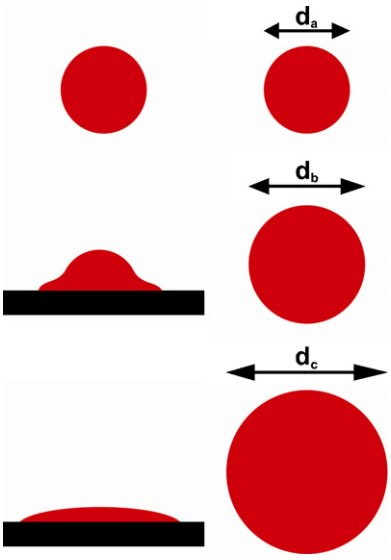

Fig. 1. Influence of non-absorbent substrate on the drop spread. The d_a, d_b and d_c represent the drop diameter after jetting (d_a) and in two stages (d_b and d_c) after hitting the substrate.

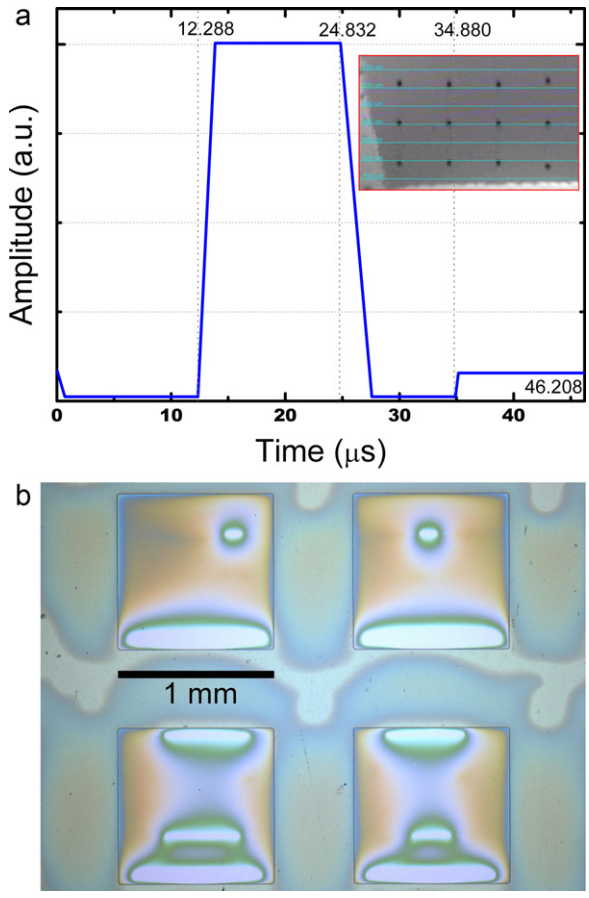

Fig. 2. (a) Waveform used in jetting experiments. The inset shows a frame captured during PEDOT jetting using ink 1 (Table 1) at 12 V firing voltage (23 kHz) and 30 °C cartridge temperature. (b) Optical microscopy (OM) showing a set of four SU8 wells filled with PEDOT-ink-1 using a 30 μm drop spacing without previous surface treatment.

Table 1
PEDOT inks developed for inkjet deposition.

PEDOT ink	Clevios P VPAL 4083 (g/mL)	% Glycerin	% Triton X-100
1	1.00	3.0	0.2
2	0.50	3.0	0.2
3	0.34	3.0	0.2

detergent, acetone and isopropanol ultrasonic baths. AFM and optical profilometry images were taken using a Nanosurf EasyScan 2 (Nanosurf AG, Liestal Switzerland) microscope and Zygo Optical Profilometer New View 500 (Zygo Co., Middlefield, USA), respectively. The AFM images were analyzed using the WSxM 5.0 Software from Nanotec Electronica S.L [13]. Static contact angle measurements were conducted to determine the wetting angle and surface energy of the samples. We employed an OCA15 plus (Dataphysics Instruments GmbH, Filderstadt, Germany) contact angle system using glycerol and *n*-dodecane [14] under ambient conditions (22 °C, RH 45–55%). For jetting experiments a commercial research grade inkjet printing, Dimatix DMP 2810, was used (Fujifilm-Dimatix, Santa Clara, USA).

2.2. Polymer wells

The polymer wells were defined by wet photolithography using negative-tone SU8 25 photoresist from Microchem Co. SU8 25 was spin-coated on 40 mm × 40 mm ITO coated glass slides in two steps at 600 rpm (5 s) and 5000 rpm (40 s). A pre-bake step was carried out for 3 min at 65 °C and then at 95 °C for 8 min on a hotplate. Then, the substrates were exposed in a near UV (350–400 nm) contact printer (Model 155, Tamarack Scientific Co., USA) for 16 s (200 mJ/cm^2) using a soft contact mask to define a 10 × 10 array of wells (each well had 1 mm × 1 mm size and 1.5 mm pitch). After exposure the substrates were submitted to a post-bake step for 2 min at 65 °C and then 95 °C for 5 min on a hotplate. The photoresist was developed in SU8 developer for 1 min then rinsed in isopropanol for 30 s and finally hard-baked at 150 °C for 5 min. The final SU-8 thickness (well height) obtained was 6.7 μm as confirmed by optical profilometer.

Table 2
Surface free energy (SFE) evaluation for ITO and SU8 before and after different surface treatments.

ITO	Surface treatment			
	Pristine	APTS liquid	APTS vapor	O_2 plasma
θ glycerol (°)[a]	65 ± 2	88.4 ± 0.5	74 ± 1	47 ± 2
θ *n*-dodecane (°)	10.2 ± 0.4	7.7 ± 0.1	7.4 ± 0.5	25.0 ± 0.4
γ_p (mN/m)[b]	24.7	2.1	7.0	23.1
γ_d (mN/m)[c]	14.8	24.9	24.9	22.8
SFE (mN/m)[d]	36.04	26.63	31.84	45.85
SU-8	**Surface treatment**			
	Pristine	APTS liquid	APTS vapor	O_2 plasma
θ glycerol (°)	79.3 ± 0.5	86.6 ± 0.2	79.1 ± 0.5	63 ± 4
θ *n*-dodecane (°)	10.9 ± 0.5	9.9 ± 0.5	10.4 ± 0.5	10.2 ± 0.3
γ_p (mN/m)	4.9	2.6	5.0	12.6
γ_d (mN/m)	24.6	24.7	24.7	24.7
SFE (mN/m)	29.6	27.3	29.7	37.3

[a] θ = contact angle.
[b] γ_p = polar component of SFE.
[c] γ_d = disperse component of SFE.
[d] SFE = surface free energy (SFE and its polar and disperse components were calculated based on the geometric mean Owens–Wendt–Rabel–Kaelble method (OWRK)) [18].