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Line printing solution-processable small molecules with uniform surface profile via ink-jet printer

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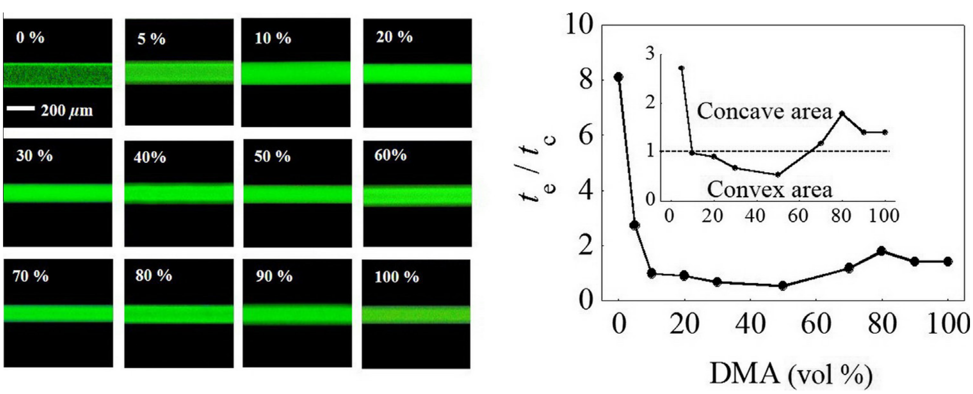
GRAPHICAL ABSTRACT



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ABSTRACT

Line printing offers a feasible approach to remove the pixel well structure which is widely used to confine the ink-jet printed solution. In the study, a uniform line is printed by an ink-jet printer. To achieve a uniform surface profile of the printed line, 10 vol% low-volatile solvent DMA (3,4-Dimethylanisole) is mixed with high-volatile solvent Pxy (p-xylene) as the solvent. After a solution-processable small molecule is dissolved, the surface tension of DMA solution becomes lower than that of Pxy solution, which creates an inward Marangoni flow during the solvent evaporation. The inward Marangoni flow balances out the outward capillary flow, thereby forming a flat film surface. The line width of the printed line depends on the contact angle of the solution on the hole injection layer.

1. Introduction

The first low-voltage, high-efficiency, thin-solid-film organic small molecule light-emitting diode (OLED) was developed in 1987 by Kodak's C. W. Tang and coworkers [1]. Up to date, almost all the active layers in small molecule OLEDs are deposited by thermal vacuum evaporation, leading to high production cost and low yield [2,3]. The first conjugated polymer light-emitting diode (PLED) was reported by Prof. Friend's group in 1990 [4]. The next year, Heeger's group introduced solution process to the OLED/PLED manufacturing [5]. In 2013, the world's first all-solution processed PLED display was developed by our group [6]. Solution-processable materials benefit from the facile device fabrication, scaling-up

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capability, compatibility with flexible and lightweight substrates, as well as easy control of their electrical and optical properties [7]. Many solution processes have been developed to fabricate OLEDs and other organic devices. Coating techniques, such as spin-coating [8,9], dip-coating [10], and blade coating [11], are utilized mainly on small size mono-color and backlighting devices. Unfortunately, almost over 95% materials are wasted or contaminated via spin-coating and dip-coating processes. Therefore, a deposition process for solution-processable materials without wasting is desired.

Printing techniques are suitable non-wasting deposition process, which mainly include gravure printing [12], screen printing [13], and ink-jet printing [14]. Different printing techniques require substantially different ink rheological properties. For example, ink-jet printing demands dilute ink solutions, while gravure printing and screen printing ask for more viscous inks [14]. The advantages of ink-jet printing lie in the accurate and convenient deposition of a wide range of functional materials in a large area at low cost, and the possibility of delivering extremely small volume solution with almost no waste of the material [15,16]. Due to the non-contact and maskless printing manner of the ink-jet printing process, the contamination of the substrate is minimized [14]. In addition, ink-jet printing can be utilized in automated fabrication process allowing selective patterning of the surface [17].

To pattern the color in a solution processed OLED display with ink-jet printing, a bank surrounding each pixel is generally built to confine the ink-jet printed droplets as illustrated in Fig. 1a. DuPont Displays developed a so-called nozzle printing to remove the well structure (Fig. 1b) from the active matrix OLED display panel [18]. Without the well structure, one photolithographic process could be saved to reduce the production cost of OLED display. However, DuPont Displays' proprietary nozzle printer is hard to access. In our contribution, we successfully developed a line printing process using an ink-jet printer. To achieve a uniform surface profile, mixed solvent of Pxy/DMA with volume ratio of 9:1 is used to dissolve a solution-processable small molecule. After dissolving the small molecule, the surface tension of DMA solution is reduced from 30.2 mN/m to 23.6 mN/m, while Pxy solution's surface tension is kept constant at around 26 mN/m. The surface tension gradient in the mixed solvent solution creates an inward Marangoni flow which balances out the outward capillary flow, thereby forming a flat film surface. By adjusting the volume ratio, the film's surface profile is changed from concave to flat to convex by the combination effect of the surface tension gradient and the viscosity of the solution. It's shown that the contact angle of the solution determines the line width of the printed line.

2. Experimental

A highly soluble amorphous small molecular material Compound 1 was synthesized in our research group recently (Fig. 2), to serve as an efficient emission material for small molecule OLEDs [19]. In the work, emitter Compound 1 was respectively dissolved in Pxy (p-xylene), DMA (3,4-Dimethylanisole), and their mixture at 10 mg/ml to make ink-jet printable inks. All the solvents with purity better than 99% were purchased from Sigma–Aldrich. Generally, to achieve high efficiency, the OLED device requires a hole injection layer (HIL or HTL). In our work, poly-(9-vinylcarbazole), PVK (Fig. 2), was chosen as the HIL. PVK with Mn = 1,100,000 purchased from Sigma–Aldrich, was first dissolved in chlorobenzene with the concentration of 8 mg/ml. The PVK solution was spin-coated on the glass substrate at a spin speed of 2200 rpm for 40 s followed by being baked at 140 °C on the hot plate in nitrogen for 30 min. Each small molecule ink was ink-jet printed through a 30 μm nozzle by a JetLab II printer (MicroFab Technologies Inc.) onto the PVK coated substrate which was heated at 45 °C. The printed films were dried in a vacuum chamber at room temperature for 8 h to remove the solvents. The surface tension and contact angle measurements were carried out by OneAttension software and an Attension tension meter at 25 °C. The viscosity of inks was obtained by a Brookfield Rotational Viscometer (LVDV-I+) at 25 °C. The thickness of films was measured by a Veeco Dektak 150 surface profilometer. The solid films' photoluminescent microscopic pictures were taken under a microscope with camera (Nikon DS-U3) by illuminating the film with a UV lamp.

3. Results and discussion

3.1. Basic theory

How to achieve uniform solid films from the ink-jet printed inks is one of the biggest challenges for ink-jet printing process [20]. The most commonly observed phenomenon is a coffee ring-like surface profile after solvent evaporation, showing that most of the solute is pushed to the edge of the droplet [21–24]. Various approaches have been explored to reduce the coffee ring effect, such as controlling the ambient humidity, mixing different solvents, adjusting the substrate's temperature, modifying the substrate's surface energy, adding the surfactant, and making special-shaped solute particle, etc. [25–32]. All the methods are based on optimizing the interactions between the evaporation-driven capillary flow and the Marangoni flow [33–35].

Evaporation-driven outward capillary flow is common for a sessile droplet with a contact angle of less than 90°, which is the root cause of the coffee ring effect [36]. The Marangoni flow is the flowing of the liquid from low surface tension area to high surface tension area, which happens if the surface tension (ST) gradient is present in the liquid. As described in the Eq. (1), the Marangoni number which represents the strength of the Marangoni flow is dependent on the ST gradient and inversely proportional to the viscosity of the solution.

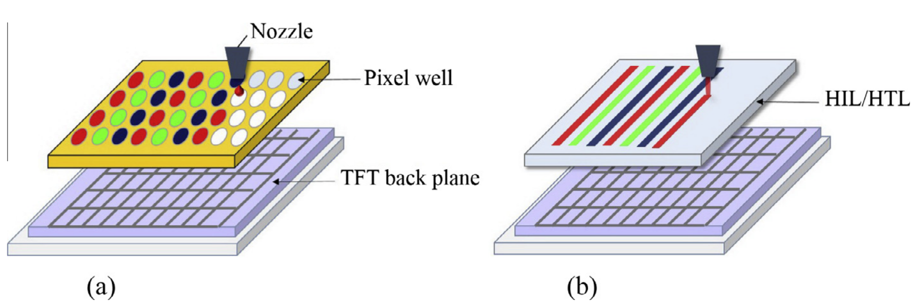

Fig. 1. (a) Schematic illustration of ink-jet printing process on an active matrix OLED display. TFT is thin film transistor. (b) Schematic illustration of nozzle printing process. The continuous printed line on the surface of hole inject layer (HIL) or hole transporting layer (HTL) removes the pixel well structure.