Evaporative Deposition of Molecular Organics in Ambient with a Molecular Jet Printer

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Abstract

We present the concept and the application of the molecular jet (MoJet) printing technique. Using this technique, we demonstrate patterned molecular organic semiconducting thin films directly printed by local evaporative deposition. Three stages are involved in the printing process. In the first stage, HP thermal InkJet printing technology is used to deliver ink drops to a micro-machined silicon membrane consisting of an array of micrometer-size pores and an integrated heater. Once the ink is filled inside the pores, in the second stage a small current is passed through the heater to completely drive off solvent from the micro-pores. In the final stage, pulsed current of larger magnitude is applied to heat up the pores to a temperature sufficient to discharge the dry ink materials out of the pores and form molecular flux. The flux is then deposited onto a nearby substrate to form designated thin film patterns.

The MoJet printing technique can be applied to pattern solution-processable molecular organic thin films, providing flux-on-demand in an ambient environment.

Introduction

Organic light emitting device (OLED) technology, considered for use in flat panel display (FPD) applications, would greatly benefit from development of a reliable, repeatable, additive deposition technique for forming patterned organic thin films, as needed in OLED applications. Today's full-color OLED displays primarily utilize white emitting OLEDs filtered by color filters to generate light emission of red-green-blue (RGB) pixels. Although this display scheme obviates the need for the challenge of RGB pixel patterning, it is a power inefficient approach to forming full-color display technology. The most efficient OLED displays would utilize patterned electroluminescent (EL) RGB layers, one color for each pixel, removing the need for color filters. Several approaches have been adopted to pattern the EL layers; among them the predominant methods include shadow masking for molecular organics and InkJet printing for polymeric materials [1].

Although the method of patterning molecular EL thin films through metal stencil masks has been around for a long time in the commercial fabrication of molecular OLED displays, there are still shortcomings. The deposition usually requires a vacuum environment. The shadow mask accumulates the evaporated material that did not reach the substrate and consequently serves as an inadvertent source of dust particles as the deposited material flakes off of the shadow mask. In the present OLED fabrication schemes, cleaning the shadow mask and the vacuum chamber contributes to significant down time of the fabrication line. Shadow masks have also proven to be not easily scalable beyond Gen3 size substrates. All these shortcomings of the shadow mask patterning step make it the bottleneck for advancement of the OLED display technology. Alternatively, InkJet technology was shown to be able to print arbitrary patterns drop-on-demand on substrates as large as Gen 8 size glass [2]. However, the pinning of the contact line of the ink drops on the substrate surface typically leads to the formation of "coffee ring stain" patterns [3], which correspond to non-uniformity in the layer thickness and are generally considered incompatible with OLED structures. For OLEDs, which are current driven devices, uniform thickness across the device is needed for uniform distribution of current density and light intensity, and consequently uniform device aging.

By combining the strengths and eliminating the weaknesses of these previous methods, we developed a new printing technique that can combine the high quality of uniform thin films provided by thermal evaporation and the reconfigurability and scalability enabled by InkJet printing.

Previously we demonstrated that a molecular jet (MoJet) printhead based on MEMS technology was successfully applied to pattern a vacuum deposited active molecular OLED [4, 5, 6]. In this article we present an improved version of this MEMS printhead and the concept of MoJet printing in ambient conditions.

Experiment

The structure and process flow of the new printhead are described in another article [7]. In brief, the MoJet chip acts as a single-nozzle micro evaporator that consists of an array of 8×8 two-micron pores and a platinum heater. As shown in Fig. 1 (a), the MoJet chip is mounted onto a ceramic socket and connected to the socket terminals with a thin layer of silver paste.

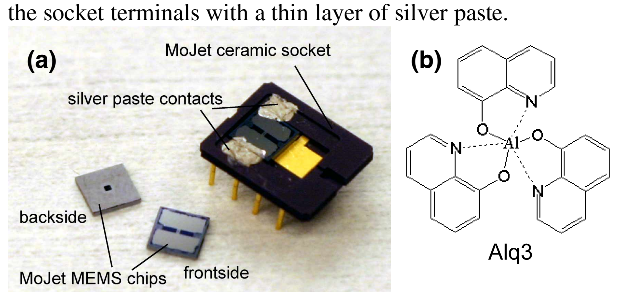

***Figure 1**. (a) MoJet printhead chips and package. The chip dimension is 4mm by 4mm. (b) Chemical structure of ink material*

We applied the MoJet technique to deposition of thin films of a molecular organic material Alq3 (tris(8-hydroxyquinoline) aluminum), which is often used as the green light emitter. The chemical structure of Alq3 is shown in Fig 1(b). 0.1M Alq3 solution was prepared and filtered through a 5µm filter into an HP thermal InkJet printhead to serve as the ink. The InkJet printhead was installed atop the MoJet printhead. A clean glass slide was attached to a moving stage to digitally translate the to-be-printed pattern image to the motion of the substrate. The glass substrate was suspended between the MoJet printhead and a video camera. The InkJet nozzle and the MoJet nozzle were aligned using this video camera viewing from underneath. The loading of ink material was controlled by the ink concentration, the volume of the InkJeted drop and the number of droplets ejected from the InkJet printer.

Fig. 2 illustrates the working principle of the MoJet printer. The printing process starts with the ejection of an ink drop from the InkJet printhead above the MoJet chip. The ink drop impinges the backside of the MoJet chip and fills the inside of the MoJet nozzle pores. A small current is passed through the integrated Pt heater to gently drive off solvent from the ink, and then a larger pulsed current is applied to heat up the nozzles to reach above the sublimation temperature of the molecular source/ejector within milliseconds [7], forming a stream of molecular flux. The molecular flux discharged out of the MoJet nozzle condenses on a near-by substrate and forms a deposited pattern. The entire process is completed within a few milliseconds. This short thermal time constant is achieved by MoJet chip design that reduces the thermal mass of the printhead.

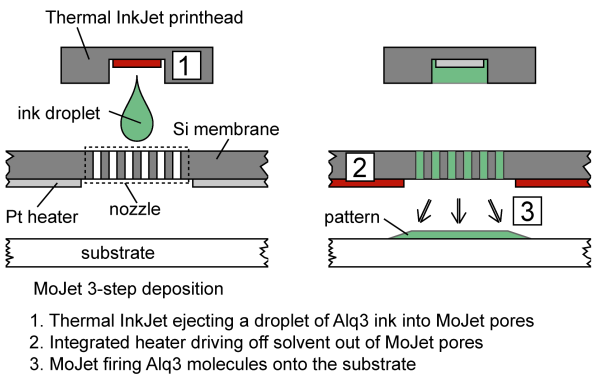

***Figure 2**. Schematic of the MoJet printer system and working principle*

Results and discussion

The performance of the MoJet heater under constant DC voltage is presented in the reference [7]. Essentially the MoJet heater behaves as a resistive heating element that converts electric energy to joule heat at the nozzle. The MoJet jetting energy is controlled with a computer controlled pulsed DC power supply. The temperature that the nozzle can reach is directly related to the jetting energy. A pulse train is generated in phase with the motion of the substrate. The jetting energy is adjustable by the DC voltage, the number of pulses in a pulse train and the length of each pulse. For typical deposition the pulse length is in the range from 1 µs to 10 ms, and the number of pulses also varies between 80 and 400.

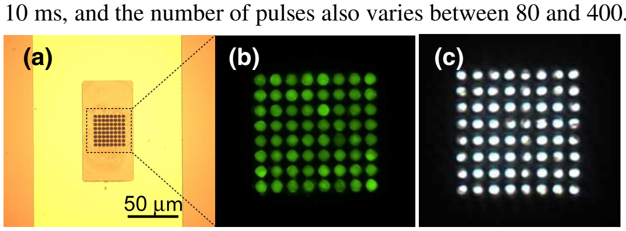

***Figure 3**. Optical microscope image of the MoJet printhead. (a) before ink loading;(b) Photoluminescent image of MoJet nozzles filled with Alq3 solids; (c) empty pores after MoJet heater firing and complete evaporation of Alq3 in pores*

Prior to the loading of ink drops in the MoJet printhead, all of the MoJet pores are empty, as seen in Fig. 3(a). The photo-luminescent (PL) image of MoJet nozzle after loading of ink and driving off of solvent is shown in Fig. 3 (b). Green PL emission is the signature of Alq3 solids presented inside the pores. The nozzles become empty again, by the intensive firing of Pt heater. This is confirmed by white light that can pass through the pores as shown in Fig. 3(c), which indicates that the MoJet printhead is ready to receive another drop of ink to repeat the same printing cycle.

During the MoJet printing process, the final pattern size is drastically influenced by the background pressure. Previously we demonstrated that a pattern size of ~30 µm can be defined in a vacuum chamber of 10^{-6} Torr by using a 25 µm silicon membrane stencil mask [4,6]. However in an ambient environment (N_2 atmosphere), frequent collisions between Alq3 molecules and nitrogen molecules will lead to broadening of the deposited pattern. Fig. 4(a) reveals the result of MoJet printing conducted at 1 atmosphere. With a 30 µm pore-array nozzle, the size of Alq3 pattern is ~60 µm. This is a broadening factor of about two for the MoJet printhead suspended 100 µm above the glass substrate surface. To define smaller feature size, it may be necessary to scale down the nozzle size or alternatively to use micro pores of larger aspect ratio to direct the molecular flux.

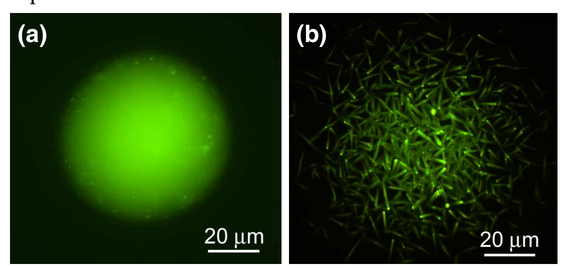

***Figure 4**. PL images of MoJet printed Alq3 patters in different conditions (a) solvent was completely driven off from the pores before the evaporation of Alq3 (b) Excessive solvent still exists while doing the Alq3 deposition*

The solvent residual in the pores also affects the geometry and topography of the printed pattern. When a spongy stopper was placed on the backside of the membrane to prevent the solvent from drying up, the deposited Alq3 patterns were found to re-crystallize from the amorphous phase in excessive solvent flux. Small Alq3 needle-shape crystals obtained by solvent vapor annealing [8] can be observed in Fig. 4(b). Further studies will continue to investigate this solvent vapor annealing effect.

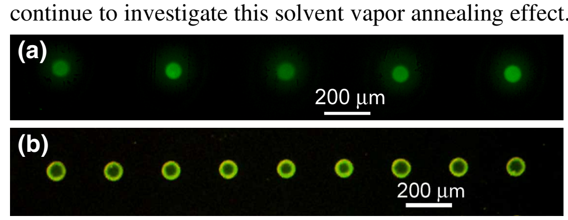

***Figure 5**. Comparison of results of (a)MoJet printing and (b)Inkjet printing*

Fig. 5(a) shows the PL image of an array of Alq3 thin film patterns of ~ 60µm diameter that were deposited 500 µm apart on a glass substrate with the MoJet printer. The same ink solution was also thermal InkJet printed on a glass substrate and the patterns were compared with the MoJet patterns. Ejected ink drops of ~150 pL volume impacted the substrate surface, spreaded to ~60 µm diameter. A PL image of typical "coffee ring" patterns is shown in Fig. 5(b), indicating a non-uniformity in the film thickness of InkJet printed films.

Summary

We printed patterned organic semiconducting thin films of Alq3 by direct evaporative deposition. The printing results were compared to those prepared by InkJet printing the same ink solution on similar substrates, showing more uniform patterns for the MoJet-printed films. The MoJet printing demonstrates the possibility of using flux-on-demand methods for patterning organic semiconductors in an ambient environment to simplify the fabrication of large-area organic electronics with high pattern precision.

Acknowledgment

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Jianglong Chen obtained his B.S. degree from Tsinghua University (Beijing, China) in 2000 and M.S. degree from Massachusetts Institute of Technology in 2003. He continued on at MIT as a Ph.D. student in materials science and engineering. His current research focuses on the direct patterning of molecular organic thin films. His goal is to develop of a more economically viable process to fabricate large-area organic electronic devices and circuits.