Printing of PEDOT:PSS for top gate organic thin film transistor

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Abstract. This report presents a thorough discussion of the DOD inkjet printing technology, including technical skills and information about Dimatix inkjet printer employed for the realisation of devices. The use of inkjet printing for the deposition of the conducting polymer PEDOT:PSS was successfully demonstrated for top gate electrode organic thin film transistors. This investigation offers a significant contribution in order to the efficient fabrication of OTFTs.

1. Introduction

The development of organic electronic devices has increased rapidly in recent times. New techniques, materials and devices structures have been used to improve device performance. For instance, various printing techniques such as inkjet, flexography, gravure coating screen and offset lithography have been implemented to fabricate polymer-based organic devices on a large scale [1]. The inkjet printing method is commonly used for fabricating organic electronic devices since it offers some potentially attractive advantages. Firstly, by using a direct-write printing process such as inkjet printing, materials are additively deposited only in the required locations. In this way, a significant cost reduction can be achieved due to process simplification and capital investment reduction as a result of reduced wastage. Secondly, the polymer devices produced by inkjet printing are friendly to the environment, because the fabrication only needs a few process steps, and it is possible to save a large amount of waste solvent and waste water by avoiding additional cleaning steps. Moreover, by solving temperature and chemical stability problems, this method provides the potential for low-temperature fabrication, enabling manufacture on flexible substrates and which can be developed with relatively low effort at laboratory scale. Because of the above reasons, inkjet printer is preferably used for organic semiconductors in organic thin film transistors (OTFTs). Furthermore, other organic devices, such as OLED-displays, both front-plane and backplane, integrated circuits and organic photovoltaic cells (OPV) have been successfully fabricated by using the inkjet printing method [2-6].

This work will include a brief discussion on the inkjet printing methodology, as well as technical skills which are used to obtain the results presented, printed Pedot PSS to produce printed gate of OTFT and printed active layer of OPV using the Dimatix inkjet printer.

2. Materials and methods

Glass substrates with pre-patterned indium-tin-oxide (ITO) were used for source and drain electrodes in the fabrication of organic thin film transistor. The channel width and length was 3 mm 20 μm respectively. 100 nm thick of P3HT active layer was deposited from the solution onto the substrate as
measured using a KLA Tencor profilometer. The performed films were then annealed by using a hot plate with a controlled temperature. For the dielectric layer, a 500 nm thick of PVP (Aldrich) was then spin-coated at 2000 rpm for 60 s. In order to remove any remaining solvent, the two-layer structures of P3HT/PVP were annealed at 85 °C in air. Lastly, PEDOT:PSS (Aldrich) as interface layer was printed or drop-cast on the top of gate PVP layer and dried on a hot plate at 40 °C in air. Immediately after drying the Pedot:PSS layer, devices characterization was conducted by using two Keithley 2400 source meters at a scan rate of 0.1 V/s in air. The relative humidity (RH) was consistently recorded as 50 ± 10% in the laboratory in which these devices characterization was measured.

3. Results and discussion

3.1. The technical skill of inkjet printing methodology

The following discussion will contain some techniques and information relating to the printer employed for the realisation of the devices discussed in this study. The DOD inkjet printing involves directing individual ink droplets through a nozzle when the application of a voltage pulse is applied to a transducer, as needed [7]. Figure 1 shows a simple schematic of the DOD inkjet system. Commonly, two basic types of actuators are employed, a piezoelectric transducer and a thermal transducer:

![Figure 1: Drop on Demand inkjet system schematic.](image1)

![Figure 2. Schematic of piezoelectric DOD inkjet printer process.](image2)
In piezoelectric DOD systems, ink is ejected from the print head using a piezoelectric material to convert an applied voltage pulse into mechanical movement inside the ink chamber. A piezoelectric inkjet print head is equipped with many single nozzles, each of which has its own ink reservoir. The mechanism of drop formation is shown in Figure 2. In the start or standby phase, depression of the ink chamber occurs by application of appropriate bias to the flexible piezoelectric crystal to prevent the ink from falling from the nozzle. When the voltage applied to the piezoelectric material is changed appropriately, the fluid in the reservoir then flows from the chamber and the displacement of the wall chamber generates the pressure to jet the ink from the nozzle. Lastly, bringing the chamber back the initial condition for pulling back the ink in the chamber and preparing the system to the next injection.

The primarily requirement of an ink to be deposited using inkjet printing is that it have the appropriate physical properties such as viscosity and surface tension [8] which impact on the mechanism of the drop formation and subsequent drop size at a given voltage [9]. Two non-dimensional numbers, the Reynolds and Weber numbers, are important quantities in order to compare and quantify ink properties. The Reynolds number is defined by the ratio of inertial forces to viscous forces within the droplet, expressed in Equation 1, and the Weber number is the ratio of inertia forces to the surface tension within the fluid (Equation 2) [9].

\[
Re = \frac{\rho v D}{\eta} \quad (1)
\]
\[
We = \frac{\rho v^2 D}{\sigma} \quad (2)
\]

where \( \eta \) is the viscosity of the ink, \( \rho \) is the density of the ink, \( D \) is orifice diameter, usually the nozzle diameter and \( \sigma \) is the surface tension.

Drop formation mechanics in DOD inkjet printing can also be analysed using a non-dimensional number \( Z \) [9-11], which is the inverse of the Ohnesorge number (Oh) [12], given by:

\[
Z = 1/Oh = \frac{Re}{\sqrt{We}} = \frac{\sqrt{\sigma \rho D \eta}}{\eta} \quad (3)
\]

where \( \eta \) is the viscosity of the ink, \( \rho \) is the density of the ink, \( D \) is orifice diameter, usually the nozzle diameter and \( \sigma \) is the surface tension. Drop formation in a DOD system only occurs when \( Z > 2 \) according to Fromm’s prediction [13]. Since the viscosity of the ink is critically dependent on its concentration, concentration also becomes an important factor in determining ink suitability.

A Dimatix Materials Printer 2800 (DMP2800) manufactured by FUJIFILM Dimatix was employed for the fabrication of printed OTFT reported in this work [14]. This printer allows the deposition of fluidic material on a substrate of maximum size 21 cm by 30 cm using a disposable piezoelectric inkjet cartridge. The vacuum platen, which holds the substrate during the printing process, does not function well when the substrate is smaller than the platen, so adhesive tape is also used to more effectively hold the substrate. The platen can be heated to up to 60 °C during the printing process. Furthermore, a drop watcher station enables manipulation of the piezoelectric jetting in order to optimise the drop characteristics during the ink injection. In addition, the drop watcher camera allows the user to directly view the jetting nozzles, the actual ink jetting and the faceplate surrounding the nozzles. The printer is also equipped with a fiducial camera, mounted on the print head carriage which allows aligning of the substrate using reference marks, setting the print origin position and measuring the feature and locations of the substrate [14]. Software provided by Fujifilm Dimatix controls these systems.
In order to produce the best quality of printing, it is important to choose the optimal printing parameters. One of these parameters is the distance between the platen and the nozzles. Calibration of the cartridge height allows printing on substrates of different thicknesses. The cartridge has 16 jetting nozzles, which are located in-line at a spacing of 254 µm and is equipped with a built-in heater that is able to heat the ink up to 70 °C. However, it is important to underline that heating of the fluid may lead to nozzle clogging, particularly when using a high volatility solvent. Therefore, for the inks used in the work presented here, the best method was found to be keeping the cartridge at room temperature.

It is possible to choose how many of the 16 jets are used in the printing process. Changing the number of nozzles used changes the precision of the process as well as the speed of the print. Using a small number of jets suits high definition of the printed pattern and high precision, for example in printing the source and drain contacts for OTFT devices with channels on the micrometre scale. On the other hand, using many nozzles leads to a quicker printing process suited for layers of material without fine detail. It is critical to choose the group of nozzles with overall best jetting performance, and this can be checked using the drop watcher camera just before printing.

The printed pattern resolution is dependent on the drop size and the head angle. Since the platen moves in the Y direction and the print carriage moves in the X direction during the printing process, the jetting nozzles moving upon the substrate follow a single line in the X direction. The head-angle determines the spacing of drops in the Y direction for a single pass of the print head in the X direction. This process produces a partial overlap of the drops which defines the print resolution. To optimise the final quality of printed devices, it is important to adjust the drop spacing which directly correlates to adjustment of the head angle. The drop spacing can be adjusted between 5 and 254 µm. Determining drop size, which depends on the jetting frequency and the firing voltage used, is also important. The drop watcher is used to inspect the drops and to define the drop radius.

Another influencing factor that needs to be carefully considered is waveform of the signal applied to the piezoelectric element. Waveform adjustment allows more precise control of the shape and the size of the droplet by changing the voltage, jetting frequency, and the slew rate, amplitude and pulse-duration of each step change in voltage. An example of a jetting waveform is illustrated in Figure 3.

The cleaning station, which is equipped with a replaceable adsorbing pad, is used for soaking up the ink from the nozzle plate. There are three primary methods can be combined in the formation of cleaning cycles: blotting, purging and spitting. Purging, pushing air out of fluid path is required to ensure that all cartridge channels are filled with no air bubbles. Blotting is required to clear any drops formed around
the nozzles. Spitting is required to clear any clogging at the orifice of nozzles. Cleaning cycles can be run before, during and after the printing process as well as during resting time.

During this investigation, some challenges have been faced such as mis-directed nozzles, non-jetting nozzles, mismatched velocities and improper alignment of the print cartridge. Mis-directed nozzles are observed when the nozzle is contaminated and/or air is present inside the nozzle. This problem can be solved by filtering the ink before filling the cartridge, checking the cleaning pad to see if it has not dried out or over-saturated or performing a purge cycle with a new cleaning pad. Illustration of misdirected nozzles is provided in Figure 4.

Non-jetting nozzles, when nozzles do not eject a drop, occur due to two possibilities: one, air is entrapped in the pumping chamber which cancels the jet pulse; secondly the nozzle could have been dried out or plugged. This problem may be overcome by a cleaning process with a good cleaning pad and/or by applying an appropriate solvent to the plate of nozzles to dissolve dried jetting fluid [15]. An example of a non-jetting nozzle is shown in Figure 5.

Adjusting the drop velocity of all sixteen nozzles is absolutely essential since this directly affects image quality. Using the drop watcher to adjust the voltage level applied to the piezoelectric element in each nozzle to make the velocity of drops ejecting from each nozzle match is the best way to avoid mismatched velocities. An example of mismatched velocity can be seen in Figure 6.

As described above, the proper alignment of the print cartridge contributes to a good quality of printed pattern. The printer software requires the user to physically rotate the head to an appropriate angle. Failure to adjust this angle accurately contributes to the presence of gaps. Figure 7 shows gaps resulted by the fault setting the angle head.

![Figure 4. Misdirected nozzles.](image1)

![Figure 5. Non-jetting nozzles.](image2)
In the next section the used of the Dimatix inkjet printer to produce printed gate of OTFTs and interface layer of bulk heterojunction of OPVs will be described.

3.2 Inkjet printing of gate electrode of OTFT fabrication
Following our successes with the fabrication of NPOTFT devices using spin coating to deposit the semiconductor and dielectric layers, in this step is to investigate the fabrication and characterization of OTFTs using drop-cast of gate electrodes and subsequently OTFTs featuring a printed gate electrodes. PEDOT:PSS is widely used as source/drain and gate electrode material in inkjet-printed polymer electronics as it has high stability, excellent submicron forming properties and high conductivity [4, 16-18]. In this study, inkjet printing is used to deposit PEDOT:PSS as the gate electrode of top gate OTFTs with the configuration illustrated in Figure 4.1. The devices operate at low voltages and show characteristics similar to those obtained with a drop-cast PEDOT:PSS gate electrode. Both $I_{on}$ and $I_{off}$ are lower for the printed-gate transistors (Figure 8 (a) and 9 (a)) than the drop-cast gate devices (Figure 8(a)), it has been shown previously that PEDOT:PSS can increase conductivity of P3HT in these devices [19]. The printed-gate devices exhibit highly reversible transfer current-voltage characteristics for devices using both a PVP (Figure 9 (b)) and PVPy (Figure 9 (b)) dielectric layer. These devices also exhibit reduced hysteresis compared with the the drop-cast gate transistors (Figure 8 (b)). We believe that a printed gate electrode provides a better way to control the area and the location of the gate electrode, therefore improving the reproducibility of the OTFT. These improvements make the devices much more applicable to applications in which device-to-device variations are undesirable, such as biosensing.
Figure 8. (a) IV curve, (b) transfer curve of an OTFT device with a drop cast PEDOT:PSS gate electrode at $V_D = 1.5$ V.

Figure 9. (a) IV curve, (b) Transfer curve of an OTFT device (PVP dielectric) with a printed PEDOT:PSS gate electrode at $V_D = 1.5$ V.
4. Conclusion
In this report, we have investigated two types of semiconducting organic thin film transistors, the use of drop cast and printing methods for top gate organic thin film transistors. A systematic discussion of the DOD inkjet printing technology, including technical skills and information about the Dimatix inkjet printer employed for the realisation of devices. We show that an inkjet-printed PEDOT:PSS gate reduces hysteresis of the OTFT device performance and improves the device reproducibility, which is crucial for biosensor applications.

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References

[1] Subramanian V et al. 2005 Proceedings of the IEEE 93(7) 1330-1338
[2] Holdcroft, S 1991 Macromolecules 24(17) 4834-4838
[3] Arias A C et al. 2004 Applied Physics Letters 85(15) 3304-3306
[4] Sirringhaus H et al. Science 2000 290(5499) 2123-2126
[5] Yi-Kang L, Han Y C and Hsiao-Ching Y 2010 Polymer International 59(1) 16-21
[6] Chesterfield R J et al. 2004 The Journal of Physical Chemistry B 108(50) 19281-19292
[7] Basaran O A, Gao H and Bhat P P 2013 Annual Review of Fluid Mechanics 45(1) 85-113
[8] de Gans B J, Duineveld P C t and Schuber U S Advanced Materials 2004 16(3) 203-213
[9] Jang D, Kim D and Moon J 2009 Langmuir 25(5) 2629-2635
[10] Reis N, Ainsley C and Derby B 2005 Journal of Applied Physics 97(9) 094903
[11] Tekin E, Smith P J and Schubert U S 2008 Soft Matter 4(4): p. 703-713.
[12] Kölpin N, et al. Journal of Materials Science 2013 48(4) 1623-1631
[13] Fromm J E IBM Journal of Research and Development 1984 28(3) 322-333
[14] Dimatix, http://www.fujifilmusa.com/support/ServiceSupportProductContent.do?dbid=881325 &prodcat=879589&ssucatid=664272.
[15] Beulen B et al. Experiments in Fluids 2007 42(2) 217-224
[16] Liu Y, Cui T and Varahramyan K 2003 Solid-State Electronics 47(9) 1543-1548
[17] Groenendaal L et al. 2000 Advanced Materials 12(7) 481-494
[18] Crispin X et al 2006 Chemistry of Materials 18(18) 4354-4360
[19] Elkington D et al. Organic Electronics 2012 13(1) 153-158
[20] Yadav S, Kumar P and Ghosh S 2012 Applied Physics Letters 101(19) 193307
[21] Kim C S et al. 2008 Applied Physics Letters 93(10) 103302