Ink Jet Printing of Functional Materials

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Abstract

Ink jet printing has been targeted as a key technology for OLED, TFT backplane and other organic semiconductor device fabrication. This presentation will concentrate on aspects of the IJ process, formulation design, jetting performance, interaction with the substrate and resultant printed device performance.

1. Introduction

Fabrication of OLED and TFT's for display applications by IJ printing involves many individual but interrelated processes. These include:

- Design of semiconductor materials.
- Development of stable formulations that can be jetted reliably.
- Design of patterned substrates together with banks, electrodes and other structures.
- Pre- and post-treatment processes to ensure correct OLED, semiconductor and dielectric layer formation.
- Optimization of deposition and drying process.

Each of these steps has to be designed to fit the complete manufacturing process, independently developed and then optimized for the total device.

In this paper we describe some aspects of this development cycle leading to commercially available ink jettable OLED, organic semiconductor and dielectric inks using polymers and small molecules for OLED, TFT and other semi-conducting device fabrication in displays applications.

2. Results and discussion

Merck has developed a number of OLED and organic semiconductor materials over recent years including amorphous and crystalline polymers [1] together with crystalline small molecules with high mobilities when applied from a spin coat formulations and fabrication process. To complement these materials, we have also optimized a range of low K spin coatable dielectric materials, self assembling monolayer treatments (SAM's), adhesion promoters and other processing aids.

OLED and OE materials designed for standard spin coat application suffer from a number of issues when it comes to ink jetting that limit their utility. The rheological properties of the inks often adversely effects the jetting process and subsequent drying and film forming processes are radically different from spinning and this can lead to 'coffee-staining' [2], different crystal morphologies and other undesired effect. These differences can result in sever device performance degradation or even no observed optical or electrical properties.

We will exemplify the optimisation of some key steps the fabrication of generic top and bottom gate OE devices as exemplified in figure 1 using the steps depicted in figure 2 and printing of OLED displays.

Fig 1. Generic top gate TFT structure

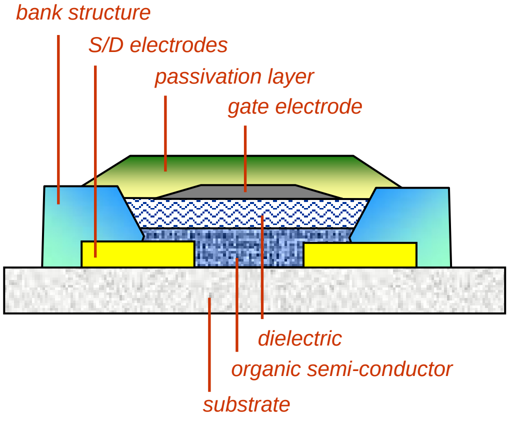
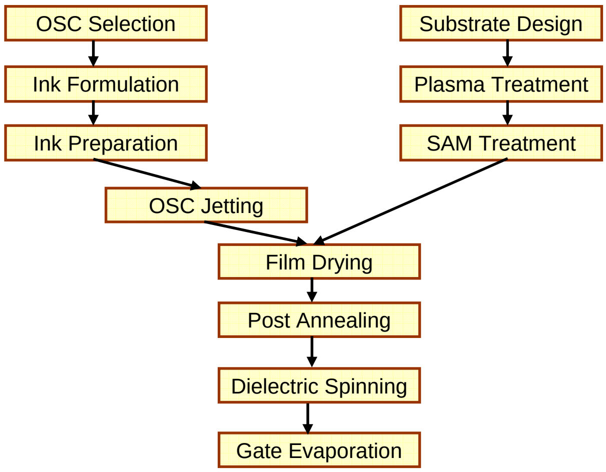


Fig 2. Stages in the fabrication of a top gate TFT



Organic semiconductors are selected based on processability, mobility, reproducibility, chemical stability and device durability.

Our first phase in development of an IJ printable ink is to define the type of ink to be used depending on the material class and application. Our preferred option is a solution phase ink, in which we may use just the functional material in a solvent or solvent blend to obtain the correct device effect, or we may add other materials to obtain enhanced performance. In exceptional circumstances we may employ dispersion based or more complex systems for example when our active material has a particularly low solubility.

Preference for a solution based ink is deliberate as it enables reliable jetting characteristics and accesses many variables which can be employed to obtain maximum and reproducible device performance.

Design of an OLED or OE solution proceeds with identification of potential solvents to dissolve the polymer or small molecule at the required concentration. Our solvent choice is determined by a number of properties with the more important ones summarised in Table 1. Inks are formulated in our preferred solvent or solvent blend with additives as required followed by optimisation based on feedback data from the down stream processing steps. Concentration is fixed to provide the target layer thickness on drying from a predetermined number of drops of known volume which is largely predefined by the IJ head that has been selected.

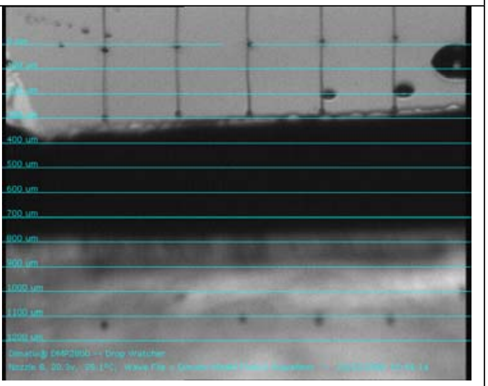
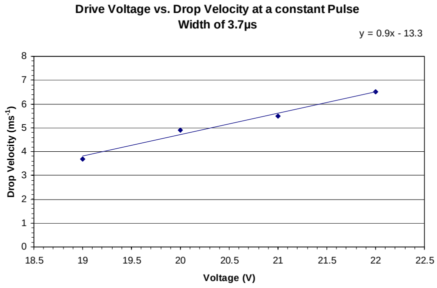
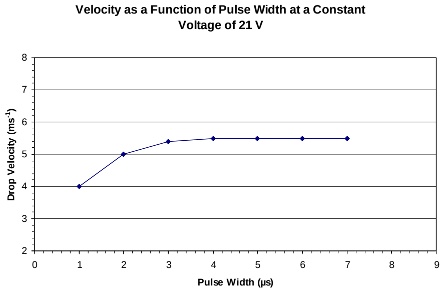
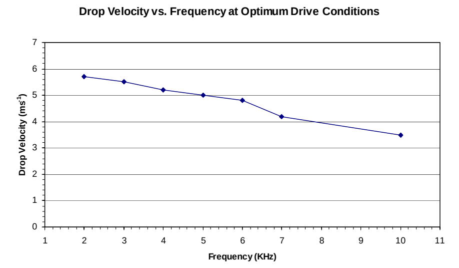
Table 1. Solvent selection for IJ printing of functional materials

Property / topic	Preferred value or parameter
Toxicity	Low toxicity. No known cacogenic, mutagenic or reproductive toxic effects
Environmental	Non-halogenated, low odour
Availability and cost	Available in litre scale production at reasonable cost
Stability	Chemically stable. No inhibitors required
Inert	No chemical and physical interaction with OLED / OSC, IJ head and printer engineering
Solvent strength	Enable > 0.5% w/w stable solution of functional material and additives
Boiling point	$>100^{o}$C and $< 300^{o}$C
Viscosity	> 2 cps and < 20 cps of ink at jetting temperature. Newtonian behaviour and minimal viscoelastic behaviour
Surface tension	> 25 dynes/cm and < 50 dynes/cm
Evaporation behaviour	Correct crystal morphology formed for crystalline materials

Care is taken over ink preparation to ensure no particle contamination. Full rheology and surface tension characterisation is undertaken and degassing is performed prior to jetting work.

Evaluation of jetting performance is undertaken to ensure accurate and reliable drop formation and head driving parameters are optimised to achieve the best possible printed devices. An example of a semi-conducting ink evaluation using the Dimatix DMP 2800 print system fitted with the 10 pl MEMs head [4] is presented in table 2. Inks which perform poorly are improved by reformulation and good inks are then further tested using our collaborators preferred IJ head.

Table 2. IJ evaluation of a functional ink

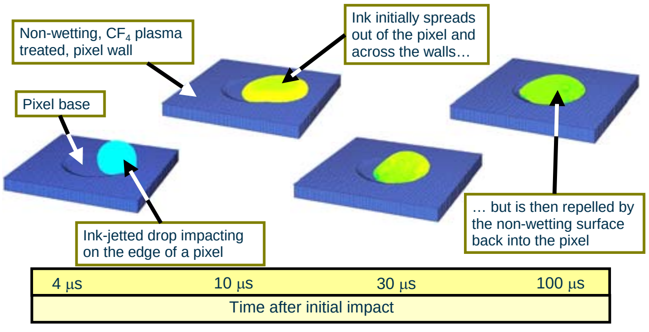
Test	Result
Summary of optimum drive conditions	Drive voltage 21V, Firing frequency 2 KHz, Pulse width 3.7 µs, Temperature 25ºC, Meniscus set point 5.0.
Indicative jetting picture	
Ligament coalescence distance	Single drops around 500 µm from the nozzle plate
Nozzle plate wetting	There was little to no wetting of the nozzle plate
Latency	All nozzles restarted after 5 min hold with no maintenance necessary
Jetting stability	Solution continued to jet stably over 40 minutes, with no loss of velocity
Drop velocity voltage sweep	
Drop velocity pulse width sweep	
Drop velocity frequency sweep	

Interaction of the drops with the substrate and controlled drying is criticality important to get the desired optical or electronic effect. Wetting and drying processes like drop movement, coffee staining [2], reticulation and reproducible crystallisation are studied and a number of different techniques used to optimise these parameters.

Many of these issues can be improved by use of pre-structured banks and/or surface energy modification of the substrate. Surface energy changes can be implemented by bank material selection, plasma or SAM treatment. We use both fluid dynamics modelling [3] and empirical testing to enhance the impact, spread and drying processes.

Figure 3 shows modelling results for an IJ drop landing on a pre-structured substrate consisting of hydrophilic centre and hydrophobic bank formed by CF_4 plasma treatment. If the drop lands off centre the hydro-dynamic forces drives the drop to areas of highest surface energy.

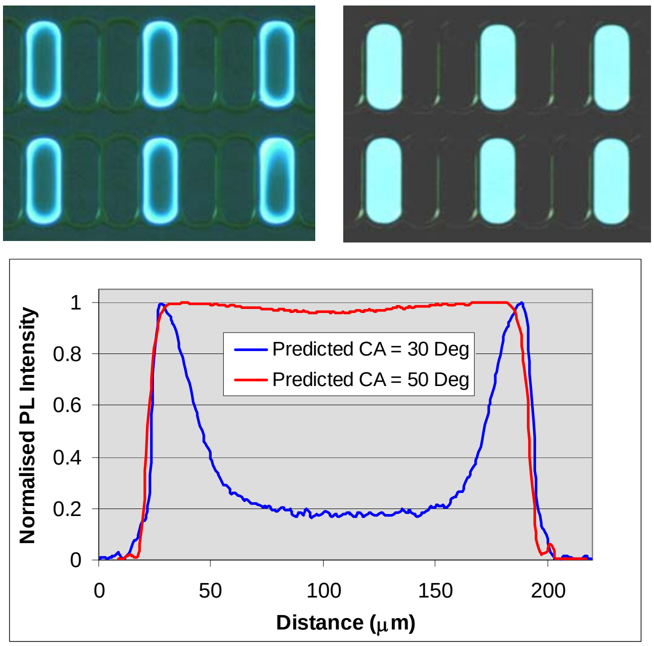
Fig 3. Self positing effect by surface energy control



These modifications can also have a big impact on the drying process and if well controlled, can stop coffee staining to provide level films. Results on our blue OLED in figure 4 demonstrate the real effect of differing the surface energy of the bank structure and the effect this has on the topology of the dry film.

Fig 4. Observed OLED drying

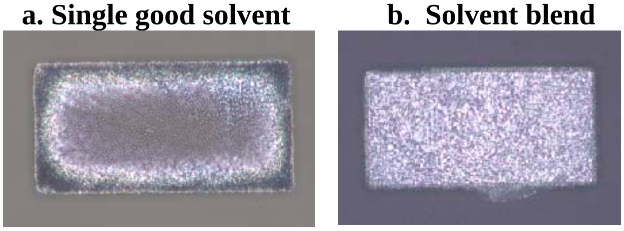
Bank contact angle 30° **Bank contact angle 50°**



Solvent and blend selection together with drying conditions employed impacts the film topography and crystal structure which in turn affects material performance. Figure 5 demonstrates an alternative way to stop coffee staining with a crystalline small molecule OSC. Structure 5a is formed by IJ deposition from a single good solvent formulation. Structure 5b is obtained from a blend of good and poor solvents.

Fig 5. Solvent selection to control coffee staining

a. Single good solvent **b. Solvent blend**



OLED displays and organic thin film transistors have been fabricated by IJ printing using the techniques described. The corresponding spin coated devices have also been fabricated as a control. These results, summarised in table 3, demonstrate that IJ printing of devices can produce performances close to that obtained using traditional spin coat fabrication.

Table 3. IJ performance vs spin coat fabrication

Device type	Spin coat	IJ print
OLED display	Uniform pixels to the naked eye	Uniform pixels to the naked eye
Amorphous polymer TFT	TG Mobility μ= 3 X 10^{-3} cm^2/VS	TG μ= 2.6 X 10^{-3} cm^2/VS
Crystalline polymer TFT	BG μ= 0.06 cm^2/VS	BG μ= 0.04 cm^2/VS
Small molecule TFT	TG μ= 1.6 cm^2/VS	TG μ= 1.0 cm^2/VS

3. Summary

Use of techniques described in this paper has enabled Merck to demonstrate a range of OLED and OE materials and formulations which can be patterned using IJ printing to build OLED and semiconductor devices, which under the correct fabrication conditions demonstrate near comparable performance to spin coated devices. These techniques together with the commercial availability of functional inks will speed up the introduction of organic printed transistor devices for displays and other applications.

4. Acknowledgements

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5. References

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