Ink Jet printable organic semiconducting materials and formulations – Combining printability, high performance and air stability

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Abstract

Fabrication of thin film transistors (TFT's) for display applications by IJ printing involves many individual but interrelated processes from the design of organic semiconductor materials (OSCs), development of stable formulations that can be jetted reliably, the design of patterned substrates together with electrodes and other structures, pre and post treatment processes to ensure correct semiconductor and dielectric layer formation together with optimization of the 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 jet printable organic semiconductor and dielectric inks using polymers and small molecules for TFT fabrication in displays and other device applications including:

What is required from OSC materials and processes?

How can we IJ print and process OSC's?

Examples of IJ printed TFT performance we obtain.

Introduction

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

Design of organic semiconductor and dielectric materials.

Development of stable formulations that can be coated printed or jetted reliably.

Design of patterned substrates together with banks, electrodes and other structures.

Pre- and post-treatment processes to ensure correct OSC 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 organic semiconductor and dielectric inks using polymers and small molecules for TFT and other semi-conducting device fabrication in displays applications.

Results and discussion

Merck has developed a number of OSC 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 and printable dielectric materials [2], self assembling monolayer treatments (SAM's), adhesion promoters and other processing aids.

OSC 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' [3], different crystal morphologies and other undesired effect. These differences can result in sever device performance degradation or even no or electrical properties.

We will exemplify the optimisation of some key steps the fabrication of a generic top TFT devices as exemplified in figure 1 using the steps depicted in figure 2.

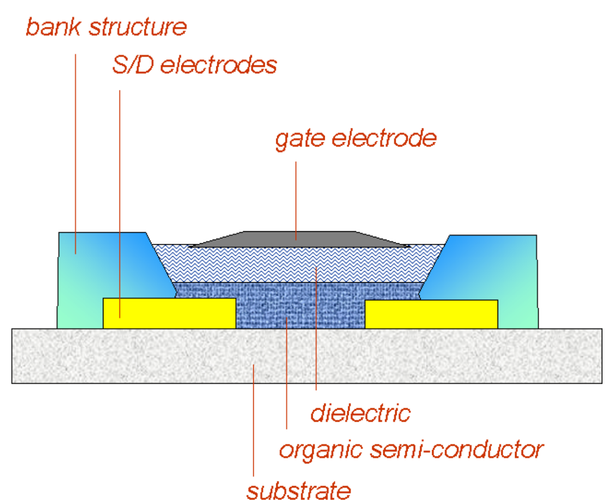


Figure 1. Generic top gate TFT structure

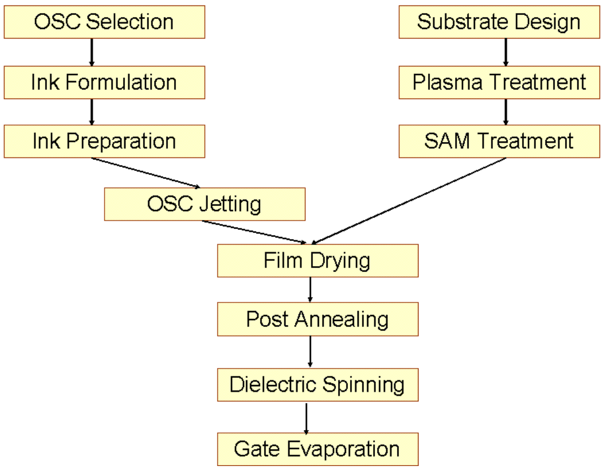


Figure 2. Stages in the fabrication of a top gate TFT

Many early OSC's suffer from issues of air and moisture stability and needed to be fabricated in inert atmospheres and the devices then encapsulated to prevent doping of the OSC by oxygen and general reactive degradation. We have employed molecular design and screening techniques to develop our high mobility OSCs with maximum processability, air stability and device durability. This enables us to process these materials and fabricate devices in standard air conditioned open laboratory or production environments with only active carbon air filtration and yellow lighting as additional protection measures.

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 OSC 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.

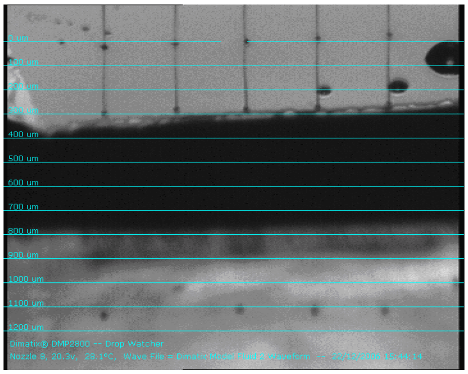
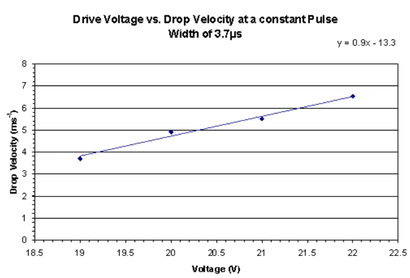
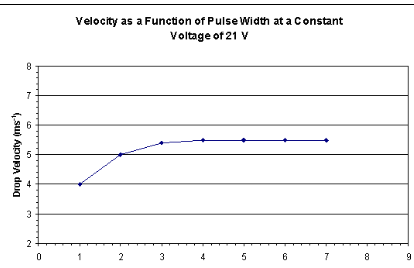
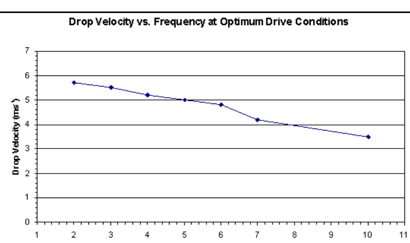
Table 1. Solvent selection for IJ printing of functional materials

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 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 with 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 [5] 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 an OSC ink

Test	Result
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	
Coalescence distance	Ligaments form a single drops around 500 µm from the nozzle plate
Nozzle plate wetting	Controlled nozzle plate wetting that did not effect jetting
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 electronic effect. Wetting and drying processes like drop movement on the substrate or on electrode structures, coffee staining [3], reticulation and reproducible crystallisation are studied and a number of different techniques used to optimise these parameters.

Some of these issues can be improved by use of pre-structured banks and/or surface energy modification of the substrate and electrodes. Surface energy changes can be implemented by bank material selection, plasma or SAM treatment. We use both fluid dynamics modelling [4] 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.

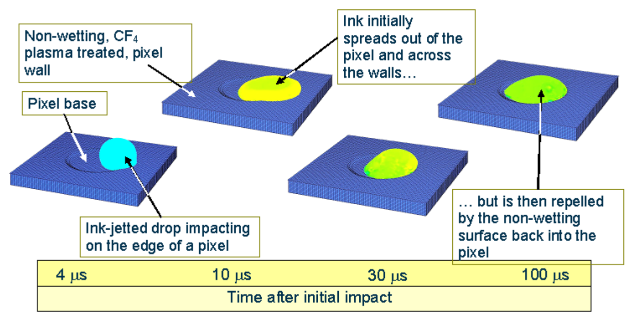
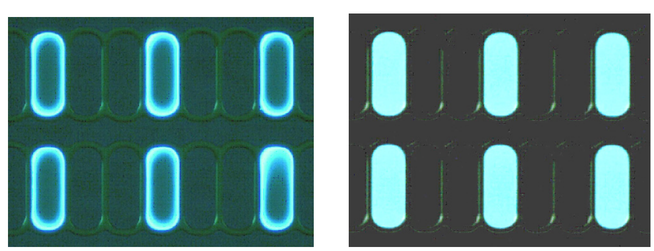


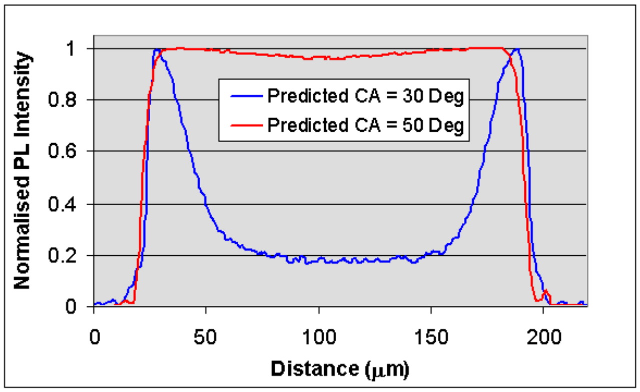
Figure 3. Self positing effect by surface energy control

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 a model amorphous polymer film formation are shown in figure 4 (a and b) [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.



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

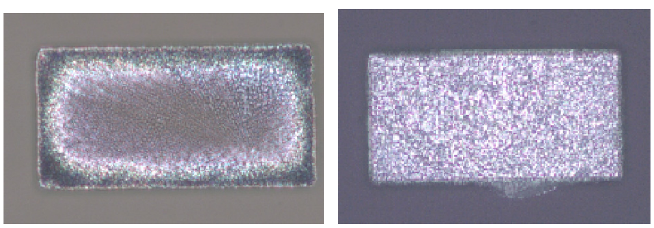
4a. Photo-luminescence image of polymer film drying



4b. White light interferometer drying profile

Figure 4. Model studies on amorphous polymer film drying

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 different solvents.



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

Figure 5. Solvent selection to control coffee staining

Organic thin film transistors have been fabricated by IJ printing using some of the techniques described.

Our high performance, organic semiconductors (S1200 class [6]) are crystalline, air stable materials. When fabricated in to a bottom gate TFT by spin coat using our matched low-K dielectric material (D180) [2, 6] on gold electrodes pre-treated with our SAM formulation (M001 [6]) yield mobilities around 0.5 cm^2/Vs. Similar results are obtained by IJ printing the OSC layer using a FujiFilm Dimatix SX3 IJ head [5] driven on a Litrex 70 series printer.

Figure 6 shows the IJ printed BG transistor performance as plots of drain current as a function of gate voltage (I-V curve) and the linear and saturated mobility as function of gate voltage. These IJ devices not only shows high mobility (0.4 cm^2/Vs), but also display a high on/off ratio (> 10^6), close to 0 V turn on with a sharp turn on and are not significantly degraded with air storage.

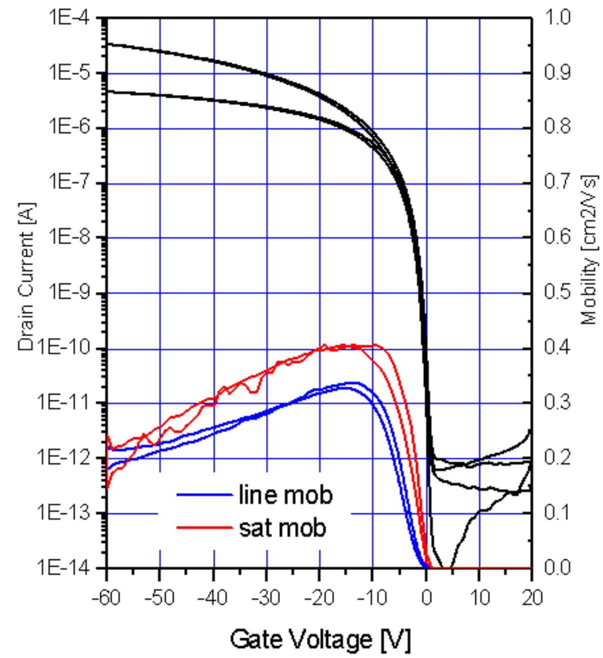


Figure 6. I-V and mobility curves for IJ Printed high performance TFT

Merck have also developed a range of 'Easy processable' polymer OSC materials (SP0300 class [6]). The amorphous nature of these materials provides greater application flexibility and ease of use but at the cost of lower mobility. Formulations are available for spin coat, IJ, flexo and gravure printing which give near identical results for given device architectures regardless of application method. Figure 7 shows the 'Easy processable' polymer TG transistor I-V curve and mobility of IJ printed devices using the widely available FujiFilm Dimatix DMP printer system. This level of performance is considered acceptable for many early printed electronic applications including electrophoretic display driver back planes.

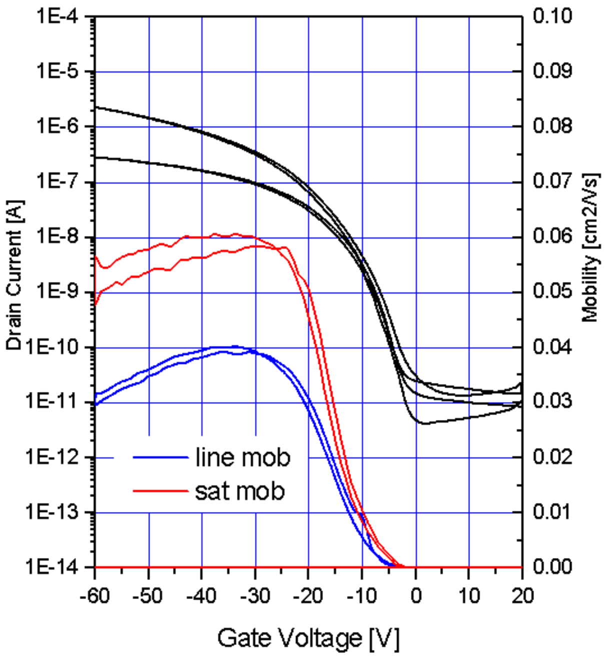


Figure 7. I-V and mobility curves for IJ printed 'easy processable' polymer TFT

Confirmation of the comparable performances of IJ printed verses spin coated devices can be found in Table 3. As a general rule, top gate performance is highest, obtaining mobilities in excess of 2.5 cm^2/Vs for our high performance materials. Bottom gate architectures are lower in mobility but offer other manufacturing benefits for example less and cheaper process steps in device fabrication.

Table 3. IJ performance vs spin coat fabrication

Device type	Spin coat	IJ print
'Easy processable' polymer TFT	BG Mobility μ= 0.015 cm^2/Vs TG μ= 0.06 cm^2/Vs	BG Mobility μ= 0.01 cm^2/Vs TG μ= 0.05 cm^2/Vs
Crystalline polymer TFT	BG μ= 0.06 cm^2/Vs	BG μ= 0.04 cm^2/Vs
High performance TFT	BG μ= 0.5 cm^2/Vs TG μ= 2.5 cm^2/Vs	BG μ= 0.4 cm^2/Vs TG μ= 2.1 cm^2/Vs

Summary

Use of techniques described in this paper has enabled Merck to demonstrate a range of high performance OSC materials and formulations, demonstrating mobilities in excess of 2 cm^2/Vs that can be patterned using IJ printing to build semiconductor devices, which 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.

Acknowledgements

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References

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[5] Supplied by FujiFilm Dimatix Inc. www.dimatix.com

[6] Commercially available from Merck Chemicals Limited.

Author Biography

Mark James received a BSc from Durham and a PhD from Newcastle-upon-Tyne, specializing in organic synthesis. After postdoctoral research at Southampton, he joined ICI and remained there for 18 years seeing the transformation through Zeneca to Avecia InkJet Limited. For 10 years he ran IJ projects ranging from colorant design to developing industrials processes to manufacture PCBs. In 2005 he moved to the Centre for Process Innovation to set up and manage their flexible electronics substrate research and manufacturing operation. Returning to IJ in 2006, Mark now leads Merck's IJ activities covering topics including OLED, OSC and PV patterning.