

# Hysteresis-free vacuum-processed acrylate– pentacene organic thin film transistors

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## Abstract

In this study, we report on the electrical characteristics of all-vacuum-processed pentacene thin film transistors, with stable and reproducible performance, using high throughput roll-to-roll processing. The method allows a polymerised tripropyleneglycol diacrylate (TPGDA) insulator layer of thickness up to 1µm to be obtained in a single pass by ultrahigh flash evaporation of monomer onto a web travelling at 10 m min<sup>-1</sup> and subsequent irradiation with an argon plasma emitted from a dc sputter cathode. From plots of  $I_D^{1/2}$  vs  $V_G$  we deduce that the resulting OTFTs exhibited a field effect mobility of 0.12 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, a threshold voltage of -21 V, a turn-on voltage of -2V, and an on/off current ratio of 1x10<sup>5</sup>. In an initial attempt to understand degradation effects and thus optimise device performance, we investigated the effect of ambient air on the I-V characteristics of our OTFTs by cycling the device-testing environment from ambient-air to vacuum and back to ambient-air. The moisture absorbed by the device during such cycling has a reversible effect on the performance of the OTFTs showing a shift in the turn-on voltage and deterioration in the on-off ratio. However, the effect was eliminated using a simple conventional encapsulation method. Our vacuum-based process thus demonstrates excellent potential for providing an alternative route to low-cost, large area organic electronics manufacturing.

## 1. Introduction

Organic thin-film transistors (OTFTs) have received considerable attention because of their relatively low processing temperatures and suitability for lightweight, flexible substrates. Among organic semiconductors, small molecules such as pentacene are a popular semiconductor material for use in OTFTs due to their high field effect mobility, which is comparable to that of amorphous Si. To fully realize their flexible properties and to facilitate the use of inexpensive plastic substrates in OTFT technology, recent interest has been directed towards the development of solution-based polymeric gate dielectrics that require low curing temperature. For example, high mobility, hysteresis-free pentacene OTFTs have been reported that utilize low temperature (110-140 °C), self-curable polyacrylate-type copolymers (L-PA) as the gate dielectric [1,2] which are compatible with conventional plastic film substrates such as polycarbonate and polyethylene naphthalate (PEN). However, spin coating and the relatively long baking time (e.g. 30 minutes) is not appropriate for a large-area, high-throughput fabrication process such as roll-to-roll (R2R). On the other hand, vacuum processing is well-known and in principle, should lead to better quality films and interfaces by negating effects such as pinhole formation during solvent evaporation and problems of depositing successive layers.

In the present study, we report on fully vacuum processed pentacene OTFTs with stable and reproducible performance using crosslinked tripropyleneglycol diacrylate (TPGDA) as the gate insulator. The TPGDA layer was obtained by flash evaporation and then subsequent plasma irradiation using a dc-magnetron sputtering target in our vacuum roll-to-roll web coating facility (see Fig.1). This new method removes the need for a lengthy anneal time and is thus fully compatible with a roll-to-roll process [3,4]. The Oxford web coater is capable of coating metals, oxides and organic layers at speeds up to 5 m s<sup>-1</sup> onto a 350 mm wide polymer web. The web coater chamber contains different deposition sources including dual

magnetron sputtering, resistive evaporation, and monomer flash evaporation deposition with an e-beam cure. By replacing the e-beam gun with the plasma of a dc- magnetron sputtering target we are able to deposit a fully cured gate dielectric layer, up to 1  $\mu\text{m}$ -thick, in a single pass (i.e., R2R) without the need for subsequent heat treatment, benefiting from being a solvent-free process.

## 2. Experimental

The key process step in the vacuum fabrication of our OTFTs is the formation of the cross-linked TPGDA gate insulator. This is achieved under vacuum by condensing a jet of the diacrylate monomer onto the substrate, (a film of PEN substrate covering a rotating drum) forming a mirror-flat finish on the substrate before the condensed liquid is plasma cured into a well-controlled, pin-hole-free polymer layer over a wide area. The optimum curing conditions for single pass experiments, i.e. the R2R mode, used in this study were 6A and  $\sim 200\text{V}$  at a delivery rate of  $4\text{ ml min}^{-1}$  and a drum speed of  $10\text{ m min}^{-1}$ . For more details about the technique refer to Ref. 5-7.

A cross-sectional diagram of the OTFTs fabricated for this study is shown in Fig.2. All devices were deposited on  $125\text{ }\mu\text{m}$  thick PEN films (DuPont Teijin Films). First, gate electrodes ( $\text{Cr/Al } 50/500\text{ }\text{\AA}$ ) were thermally evaporated through a shadow mask. Then, TPGDA polymer dielectric layers of thickness in the range  $500\text{-}1000\text{ nm}$  were evaporated using the vacuum roll-to-roll webcoating facility. Next, pentacene powder (Aldrich, as-received) was thermally evaporated onto the acrylate layer. During the deposition of pentacene, the substrates were held at room temperature. Pentacene stripes, approximately  $600\text{ }\text{\AA}$  in thickness and  $2\text{ mm}$  in width, were obtained at a deposition rate of  $\sim 0.5\text{ }\text{\AA s}^{-1}$  through a shadow mask at a working pressure of  $5\times 10^{-3}\text{ mbar}$  in a  $\text{N}_2$  atmosphere. Finally, Au source and drain electrodes were thermally evaporated on top of the pentacene strips using a

third flexible shadow mask with varying ratios of channel length,  $L$ , to width,  $W$  ( $L = 50 \mu\text{m}$  to  $150 \mu\text{m}$  in steps of  $50 \mu\text{m}$  with two different  $W/L$  ratios of 20 and 40).

The current-voltage characteristics of the OTFTs were measured at room temperature in the dark under ambient and vacuum ( $1.3 \times 10^{-5}$  mbar) conditions using Keithley 2400 units.

### 3. Results and discussion

Figure 3 shows representative (a) output and (b) transfer characteristics for non-encapsulated flexible pentacene OTFTs measured under different environmental conditions. In this case, for convenience, the cross-linked acrylate gate dielectric was prepared in with multiple passes of the plasma. Freshly prepared OTFTs were initially measured in ambient air, then stored in an air-exposed ambient for two weeks and re-measured after four hours under vacuum. In Figure 3(b) we also show the results of a further measurement taken after the device had been exposed to air for an additional six weeks. In all cases, the output characteristics are linear at low drain voltage,  $V_D$ , with clear saturation at higher  $V_D$  as predicted by the conventional transistor equations:

$$I_D = \frac{W}{L} \mu C_i (V_G - V_T) V_D \quad V_D \ll (V_G - V_T) \quad (1)$$

and

$$I_D = \frac{W}{L} \mu C_i \frac{(V_G - V_T)^2}{2} \quad V_D \gg (V_G - V_T) \quad (2)$$

where  $W$  and  $L$  are respectively the width and length of the channel,  $\mu$  the effective mobility in the channel,  $C_i$  the capacitance per unit area of the gate dielectric,  $V_G$  the gate voltage and  $V_T$  the threshold voltage.

In Table 1, values of mobility and threshold voltage estimated from the linear section of the  $I_D^{1/2}$  vs  $V_G$  plots in Figure 3(b) are reported. As can be seen in Figure 3(a), higher saturation currents are observed in ambient air but this does not reflect a higher mobility, which is  $\sim 6 \times 10^{-2} \text{ cm}^2/\text{Vs}$  in all cases, rather they arise from a positive shift of  $V_T$ . The shift in

$V_T$  probably arose from a surface polarization effect caused by water molecules. Such a phenomenon has been reported earlier for pentacene OTFTs employing a poly(4-vinyl phenol) dielectric thin film [8], and will be discussed in more detail later.

For characteristics measured under vacuum conditions, a substantial decrease in off-current,  $I_{off}$ , was observed:  $I_{off}$  decreased by some two orders of magnitude from  $2 \times 10^{-9}$  A to  $1 \times 10^{-11}$  A. Simultaneously,  $V_T$  shifted from -11V to -18V while the turn-on voltage,  $V_{to}$ , shifted from 6V to 0V. However, after storing the OTFT in an air-exposed ambient for an additional six weeks, both parameters, measured in ambient air, regained their initial values:  $I_{off}$  increased again to  $9 \times 10^{-10}$  A, while  $V_T$  and  $V_{to}$  shifted positively:  $V_T$  from -18V to -11V and  $V_{to}$  from 0V to 6V. This completely reversible behaviour indicates that these phenomena are related to the effect of reversible absorption in the devices (e.g. of water) [9, 10] rather than a permanent degradation. It is interesting to note that in this non-encapsulated pentacene OTFT device no hysteresis was observed in the transfer characteristic either in air or under vacuum.

It is well-known that many polymer dielectrics inherently contain a large number of hydroxyl groups in the film which could act as charge traps causing hysteresis that leads to a shift in  $V_T$  depending on the direction of the gate voltage sweep [11-13]. In addition, a hydrophilic and polar surface is highly affected by impurities such as moisture, oxygen or mobile charges, which are known to cause instabilities in OTFTs [14,15]. Therefore, the negligible hysteresis obtained in our OTFTs measured in ambient air is an indication that the amorphous TPGDA gate dielectric, which contains no hydroxyl groups in its fully-polymerized chemical structure, was properly cured by the plasma without requiring crosslink agents or post deposition annealing [11]. The high off-state current observed in air after a period under vacuum (Fig. 3(b)) probably arose from an increase in the parasitic source-drain current owing to the absorption of  $O_2/H_2O$  in the pentacene. This will be

exacerbated by water absorption within the gate dielectric leading to the enhancement of ionic currents. The positive shifts in  $V_T$  and  $V_{to}$  likely arise from the creation of negatively charged trap states due to the adsorption of  $H_2O$  and possibly  $O_2$  at the semiconductor/insulator interface. The partial neutralization of an existing positive interface charge by negative charges trapped on these atmospheric adsorbates would cause hole (positive charge) accumulation to occur more easily in the channel and, hence, an earlier turn-on with a more positive  $V_{to}$  and  $V_T$  is expected [11,13]. Thus, higher saturation currents are obtained in air for a given  $V_G$  than in the case of vacuum measurements. The recovery in  $V_T$  and  $V_{to}$ , after exposing the OTFT to ambient air indicates that while the contribution of  $H_2O$  and  $O_2$  to increased channel and leakage currents is significant, irreversible oxidation of the pentacene does not occur as evidenced by the reversibility of the vacuum/air results and the almost unchanged mobility before and after exposure to ambient air [8].

Kumaki *et al.* observed a positive threshold voltage  $V_T$  shift in both  $p$ - and  $n$ -type OTFTs, employing  $SiO_2$  as a dielectric, after inserting either ambient or dry air in the evacuated measurement chamber [16]. However, the  $V_T$  shift did not completely recover after pumping down the chamber. In this case the positive  $V_T$  shift was attributed to the deprotonation of  $SiOH$  on the gate-insulator surface, induced by the adsorption of  $H_2O$  and  $O_2$ .

Our results demonstrate the following: (i) The hysteresis-free performance of un-encapsulated all-vacuum produced OTFTs incorporating the dc plasma-cured dielectric TPGDA when compared with OTFTs prepared from spin-coated polymer dielectrics, and (ii) the significant increase, under ambient testing, in gate off-current and the shift in  $V_T$  are both reversible and thought to be caused by  $H_2O$  and/or  $O_2$  diffusing into grain boundaries in the pentacene film.

These results demonstrate also the importance of encapsulating the pentacene devices in order to maintain a high on-off current ratio. In an initial attempt, we have used a simple laboratory-encapsulation approach in which the devices were encapsulated, in ambient air, by a glass cover slide sealed with paraffin wax. Typical transistor characteristics from pentacene OTFTs with the TPGDA dielectric layer flash-evaporated in a single pass at a drum speed of  $10 \text{ m min}^{-1}$  are shown in Fig. 4 for three devices with a common Al gate. As seen in figures 4b and 4c, again they exhibit very little hysteresis. The off-currents in these encapsulated devices are more typical of those seen under vacuum, i.e. of the order tens of pA, leading to on/off current ratio as high as  $1.9 \times 10^5$ . The encapsulated devices, with a common gate, showed a constant negative  $V_{to}$  value of about -2V (see Fig. 4d) meaning that the transistors are completely switched off at zero gate bias. These particular devices showed moderate mobility  $\sim 0.12 \text{ cm}^2/\text{Vs}$ , which is most probably due to the deposition of pentacene thin film at low vacuum compatible with the web coater environment. This could be substantially improved by modifying the interfaces, for example, by evaporation of a buffer layer [17]. Using R2R thermal evaporation as a technology for mass production of organic electronics based on flash evaporated polymer dielectrics and small-molecule active materials could be an alternative for the solution-processing large-area printing.

#### 4. Conclusions

We have demonstrated a vacuum-based R2R-compatible polymer curing process which produces pinhole-free insulating films deposited at room temperature and which can be incorporated into the manufacture of OTFTs deposited in vacuum at high webspeed. In the process, a dc sputtering cathode is employed as a plasma source for the polymerization of flash evaporated TPGDA to form the gate dielectric layer in bottom gate pentacene OTFTs. All devices showed typical output/transfer characteristics with negligible hysteresis in both

ambient air and vacuum environments. A simple encapsulation process in air following deposition leads to devices with on/off ratios in excess of  $10^5$ . We are now further developing the process, investigating the incorporation of higher mobility semiconductors and extending the work to the manufacture and simulation of inverters and logic circuits.

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Table 1: Values of mobility and threshold voltage estimated from the  $I_D^{1/2}$  vs  $V_G$  plots and turn-on voltage estimated from  $\log(I_D)$  vs  $V_G$  in figure 3.



## Figure Captions

*Figure 1:* (Colour online) Oxford's roll-to-roll vacuum web coating facility including (a) multiple sources and (b) drum, winding and unwinding sections.

*Figure 2:* (Colour online) (a) A schematic cross-sectional diagram of the bottom gate (BG) top contact (TC) pentacene FET device architecture used in this study.

*Figure 3:* (Colour online) Comparison of ambient air vs. vacuum measurements of (a) output and (b) transfer characteristics of as-deposited and aged pentacene OTFTs fabricated with TPGDA gate films flash-deposited and cross-linked with a dc-sputtering cathode plasma using a multiple pass process.

*Figure 4:* (Colour online) Performance of pentacene OTFTs with TPGDA gate dielectric layer cross-linked in a single-pass through the dc-plasma. (a) An optical micrograph of a set of 3 source drain electrodes with channel length,  $L$ , of 50, 100 and 150 $\mu\text{m}$  and a  $W/L$  ratio of 20. (b) Typical transfer characteristics for three OTFTs with identical  $W/L$  ratio of 20. The gate-to-source currents are  $< 1 \text{ nA}$ . (c) Typical output characteristics showing negligible hysteresis. (d) Transfer characteristics plotted as  $\sqrt{I_D}$  vs  $V_G$  indicating that the threshold voltage is -21V.

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Table 1:

	Mobility ( $\mu$ ) $\text{cm}^2/\text{Vs}$	Threshold Voltage ( $V_T$ ) V	Turn-on Voltage ( $V_{to}$ ) V
Air (As prepared)	$6 \times 10^{-2}$	-11	6
Vacuum (2 <sup>nd</sup> week)	$6 \times 10^{-2}$	-18	0
Air (8 <sup>th</sup> week)	$6 \times 10^{-2}$	-11	6

Figure 1

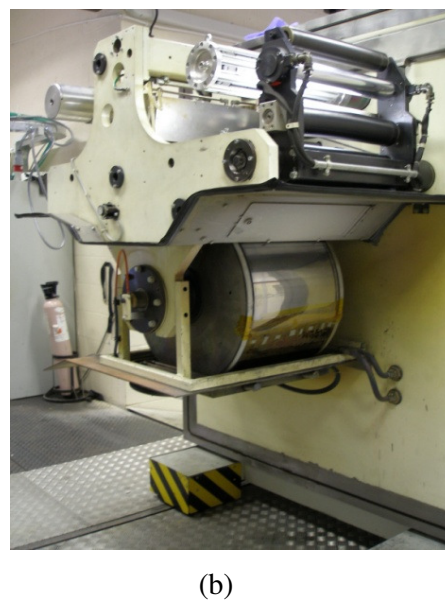
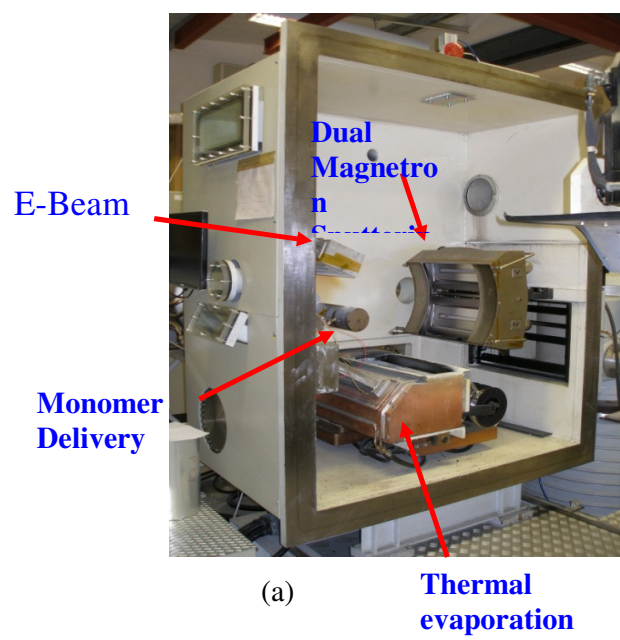


Figure 2

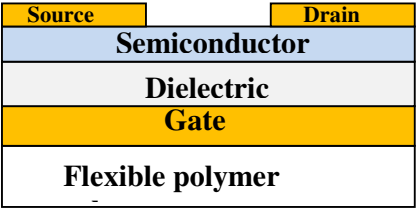


Figure 3

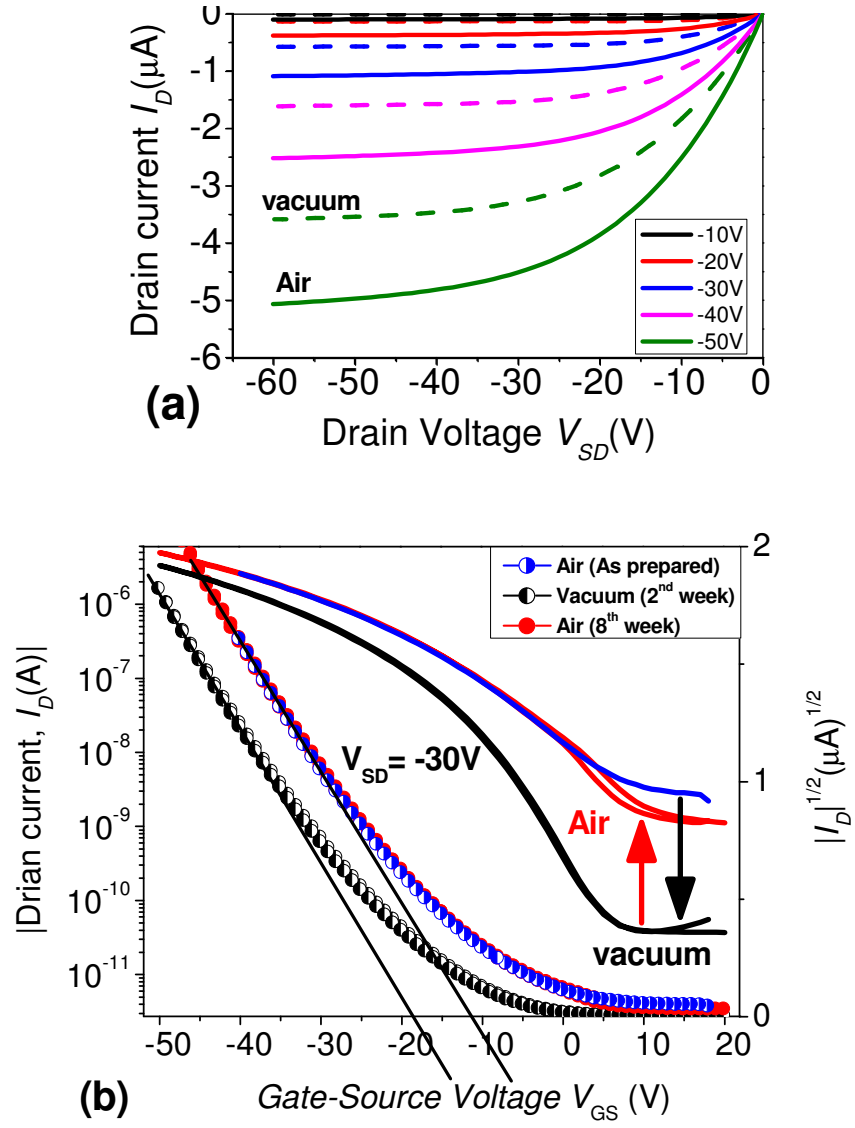


Figure 4

