

Inkjet Printed Organic Transistors for Sustainable Electronics

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Abstract

Embedded paper electronics is a promising solution for the future of electronics, and thus the goal for this paper is to show the pathway toward achieving inkjet solutions for the realization of complex circuitry on the cheapest synthetic material made by humankind: PAPER. A direct write technology, inkjet printing transfers the designed pattern directly to the substrate. Inkjet technologies have gained a lot of ground as a more accurate and economic fabrication method than traditional lithography. The challenge of this work is to identify the right materials and to show the printability of all the building blocks of an organic field-effect transistor (OTFT). For the semiconductor, a highly soluble pentacene precursor, 13,6-N-Sulfinylacetamidopentacene, is proposed. Anisole, a high boiling point solvent is chosen to insure proper jetting of the solution. The solution jets well and it has to be used right after preparation as its printability degrades with time. For the gate dielectric, two solutions are proposed: (i) using the paper itself as an insulator and print a bottom gate device on both sides of a double sided glossy paper, (ii) a pentacene impurity, of 6,13-pentacenequinone (PQ), in a top gate configuration, which may improve the device mobility by reducing the scattering sites at the semiconductor-dielectric interface. For the electrodes, a printable nano-particle based silver ink has to be modified to match the work function with pentacene, or replaced with an alternate printable material like Carbon Nanotubes (CNTs). Preliminary electrical testing of the pentacene film printed directly on paper shows good conduction properties for a 25 μm channel length. Further improvement of the pentacene film performance is proposed. This work establishes the foundation for the first fully printed OTFT on paper.

Introduction

Green electronics are becoming the new paradigm of the 21st century. The challenges faced to achieve them include battery-less systems, which scavenge natural occurring energies like solar, thermal, vibrational and pressure to replace highly polluting batteries, organic materials, as well as the use of recyclable and biodegradable substrates to replace plastics. This work focuses on the utilization of ultra-low-cost paper substrates for the realization of environmentally-friendly, all organic, inexpensive integrated circuits, an essential part of any electronic system. Printed paper electronics is a promising solution for the future of electronics. The goal for this study is to show the pathway toward achieving inkjet solutions for the realization of integrated circuits on the cheapest synthetic material made by humankind: PAPER. The challenges of this project are to identify the right organic materials to be inkjet printed with good mobility in order to produce a competitive OTFT.

A multitude of criteria are to be considered when choosing the materials: high mobility for circuit speed, low intrinsic conductivity (for high $I_{\text{on/off}}$ ratios), good stability (to oxygen, light, temperature, and humidity), solution coatability, printability and compatibility with other device components. Mobilities for existing materials suited to printing vary from more than $10 \text{ cm}^2/\text{Vs}$ for printable Carbon Nanotubes (CNTs) [1-2] to about 10^{-3} - $10^{-1} \text{ cm}^2/\text{Vs}$ for organic polymers [3-4]. A summary of the mobility values of various technologies is presented in Table I.

Well-aligned single wall nanotubes (SWCNT) arrays have shown drift mobility at device level as high as 1000 - $10,000 \text{ (cm}^2/\text{Vs)}$ [5], which is similar to or even better than silicon compounds. However, a CNT transistor requires purely semiconducting SWCNTs, that are expensive to separate and extremely difficult to integrate.

Table I. Mobility values for various technologies

Material	Mobility (cm^2/Vs)
<i>n</i> -type Si	<1500
<i>p</i> -type Si	<500
Poly-Si	100~150
Amorphous Si	~1
Organic (smallmolecules)	<5
Organic (polymer)	10^{-3} - 10^{-1}
Transition metal oxide	<200
Printable Carbon	>10

This paper will focus on organic semiconductors, more precisely pentacene. Although various carbon derivatives containing delocalized electrons such as rubrene or tetracene have been studied for semiconductor applications, intensive research has proven that pentacene is a more viable solution. Pentacene's high processability makes it a very promising material for solution-processing and printing. However, its mobility in device level measurements has been reported to be less than 0.1 - $1 \text{ (cm}^2/\text{Vs)}$ with the highest value of $2.2 \text{ cm}^2/\text{Vs}$ for purified pentacene [6], while its highest bulk mobility has been reported around $35 \text{ (cm}^2/\text{Vs)}$ [7]. The interfacial scattering in the device level and the high sensitivity of the materials reduce the mobility of Pentacene in the device level. Replacing the gate dielectrics with ordered films such as 6,13 - Pentacenequinone can reduce the scattering, resulting in enhanced mobility [7]. Reduced scattering is achieved by increasing the interfacial coherency between the pentacene crystals and the dielectric. Changing the dielectric thickness is another parameter to control the mobility. We anticipate that

this methodology at the device level could lead to mobility values over $5\text{cm}^2/\text{Vs}$.

There is increasing interest today in using organic semiconductors in inkjet printed solutions on paper substrates. Inkjet printing, as a direct write technology, transfers designed patterns directly to a substrate. Due to its capability of jetting one single ink droplet in volumes as low as 1 pl, inkjet printing can print high resolution patterns in a single step process. The choice of paper as the substrate material presents multiple advantages and has established paper as one of the most promising materials for disposable electronics applications: it is widely available, and the high demand and the mass “reel-to-reel” production make it the cheapest material ever made. Furthermore, the environmentally friendly features of the paper make it extremely suitable for green electronic applications. Previous work has demonstrated the successful development of an inkjet-printed RFID module on paper [8]. The next steps involve the integration of all the components of the sensor node; namely the printing of the sensor, which was successfully completed [9], the integration of the active devices like the integrated circuit (IC), and the batteries/power scavengers. This paper establishes the ground of the IC integration on paper by addressing the printability of active devices like a field effect transistor.

Pentacene has been previously used for field effect transistors, with a preference for 6,13-bis(triisopropylsilyl)ethynyl (TIPS) pentacene [10-11]. TIPS advantages include high solution processability which is crucial for inkjet printing, and better stability. Also previous work shows the use of paper, both as a substrate [12] and gate dielectric [13]. However, no fully printed transistor has been reported yet. This paper establishes the foundation for the first fully inkjet printed organic field effect transistor on paper.

Materials and approach

1. Semiconductor

The goal of this work was to drift away from the well-known TIPS pentacene and explore alternate materials which can provide higher performance. After careful consideration, a pentacene precursor, 13,6-N-Sulfinylacetamidopentacene, from Sigma Aldrich was chosen, with the structure shown in Figure 1. The pentacene precursor is highly soluble ($>50\text{mg/ml}$) in apolar solvents and, after being printed in a thin film is converted to pentacene by curing in nitrogen atmosphere for 5-15 minutes at $120\text{-}200^\circ\text{C}$. According to Sigma Aldrich, the OTFTs fabricated from this precursor showed the best performance of all solution processed organic semiconductors.

A very important aspect in the inkjet printing of the soluble semiconductor is the choice of the solvent. Various studies [11,14] show that a high boiling point solvent is desired to avoid super saturation of the solution and subsequent crystallization, leading to clogging of the nozzle during the printing process. Due to its lower health rating compared to chlorobenzene and toluene, and a relatively high boiling point (155°C), anisole was chosen as the solvent.

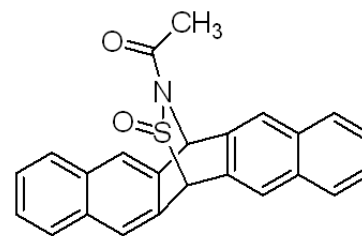


Figure 1.13,6-N-Sulfinylacetamidopentacene

The saturated solution of pentacene precursor and anisole was prepared in the dark and in nitrogen environment. The Dimatix Materials Printer DMP-2800 equipped with DMCLCP-11610 printer head was used to eject the pentacene solution droplet. 60 layers of the semiconductor were jetted at room temperature directly on Kodak photo paper with no surface preparation. The film was jetted with a 10 pl cartridge and the drop spacing was $25\ \mu\text{m}$. The voltage used for jetting the solution properly was 17 Volts. After printing, the precursor was converted into pentacene by curing the sample under nitrogen at 150°C for 10 minutes. A picture of the pentacene before and after curing is shown in

Figure 2.

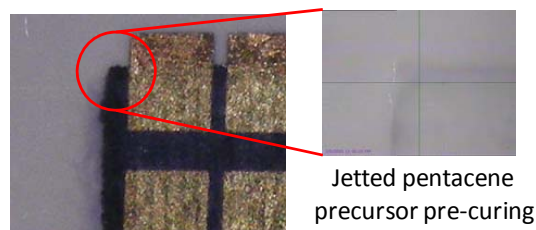


Figure 2. Cured pentacene on paper with detail of the transparent jetted precursor (60 layers) before curing

The next step was the investigation of the wettability of the silver ink with the pentacene solution. One layer of pentacene was printed on top of the silver electrodes and cured. Figure 3 shows a picture of the printed pentacene layer on the top of silver ink, with a close-up of the channel.

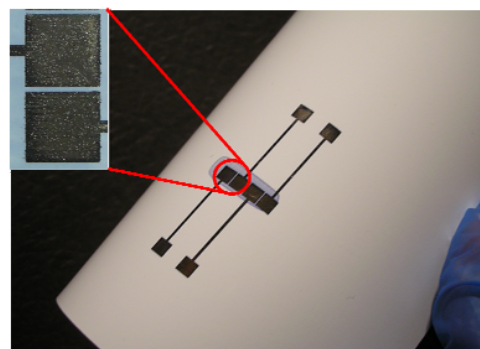


Figure 3. One layer of pentacene on top of silver electrodes

An important observation about the printability of the pentacene precursor solution is that the solution is best printed immediately after preparation. This is likely caused from

solvent evaporation from the cartridge creating a supersaturated solution. As pentacene precursor crystallites form they have the tendency to clog the printing nozzle.

2. Gate dielectric

There are two proposed solutions for the transistor configuration, presented in Fig. 2 (a) and (b) respectively.

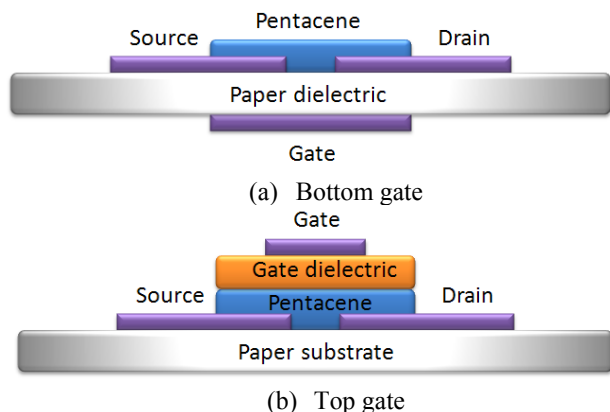


Figure 4. Proposed transistor configurations

In the first proposed solution, the paper itself is used as a dielectric. This approach has the evident advantage of less material deposition required, as the paper serves as both mechanical support and gate dielectric. The downside of this configuration is the relative large thickness of the paper which will affect the proper functioning of the device, as well as the challenge of aligning properly the top and the bottom part of the circuitry on the double sided glossy paper.

For the second solution, a gate dielectric has to be jetted as well. Reference [7] shows a method to improve the mobility of a pentacene device using a layer of 6,13-pentacenequinone (PQ), which is known to be the most common impurity present in pentacene. The interface between the pentacene and the PQ helps reducing the scattering sites and therefore improves the device mobility. Furthermore, PQ is an insulator with a measured dielectric constant of 3.5 [7], satisfactory for the gate dielectric. Therefore, the solubility and printability of the pentacene impurity were investigated in this work.

The same solvent, anisole, was used to disperse the 6,13-pentacenequinone with good results. The solution jetted well and it showed better stability with time than the pentacene precursor solution. A picture of the printed PQ on top of two silver electrodes, as well as a standalone square 60 layers thick directly on paper are shown in

Figure 5.

1. Electrodes

Electrode material selection for organic transistors is hard because the electrodes' work function must be greater than the highest occupied molecular orbital (HOMO) of the semiconductor. Silver electrodes are easily patterned with a commercial nano-particle ink from Cabot followed by a 140°C sintering, creating a reliable conductive surface. Unfortunately, silver has a work function of only 4.3eV, not enough compared to the HOMO of pentacene 5.07eV [15].

Although silver electrode based TIPS pentacene transistors have been reported with a device mobility of $0.07 \text{ cm}^2/\text{Vs}$ for a channel length of $33 \text{ }\mu\text{m}$ [3], the conduction is expected to be poor and the performance of the device to be degraded. Future work will present alternative solutions like surface modification of the printed Ag electrodes for increasing the work function or use of other printable conductive materials like carbon nanotubes (CNTs) [9].

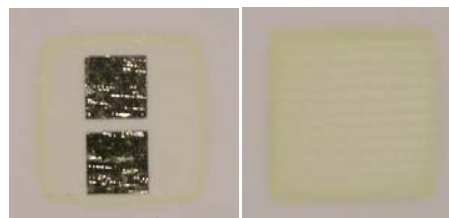


Figure 5. Printed 6,13-pentacenequinone on paper

Testing and characterization

After the successful printing and curing of the pentacene, its electrical characteristics were measured in order to validate the process before moving to the device level. The pentacene film was exposed to air and light for about 2 weeks before testing and placed back in nitrogen about 24 hours before testing. Measurements of the IV curves have been carried out inside a nitrogen-filled glove box using an Agilent E5272A source/monitor unit.

The method used was the transmission line method (TLM) [16], involving deposition of electrodes on top of the pentacene layer with various gaps and measuring the current between the two electrodes through the pentacene film. From the plot of the resistance values vs. the gap, the contact resistance and the surface resistivity are extracted. Since the method involves no gate bias, we chose Au electrodes due to the compatibility between the pentacene bandgap and the gold work function of 5.1 eV. Au electrodes were deposited through a shadow mask by thermal evaporation at 10^{-6} Torr and a rate of $1 \text{ }\text{\AA}/\text{s}$. A picture of the thermal deposited gold on the top of the pentacene film on paper is shown in Figure 6. The dimensions of the TLM patterns for the indicated row in Figure 6 were: $w = 1.2 \text{ mm}$ (electrode width), $l_i = 25, 50 \text{ }\mu\text{m}$ (channel length).

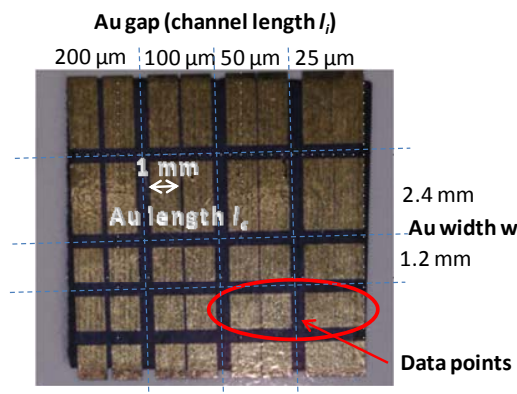


Figure 6. Au deposited for TLM resistivity extraction

The IV curve was well defined for 25 and 50 μm channel lengths, while for 100 μm it was not possible to have

consistent data due to the very high resistivity of the semiconductor or to the non-homogeneous film.

Figure 7 shows the measured IV characteristics obtained for the first two channel lengths of 25 μm (a) and 50 μm (b).

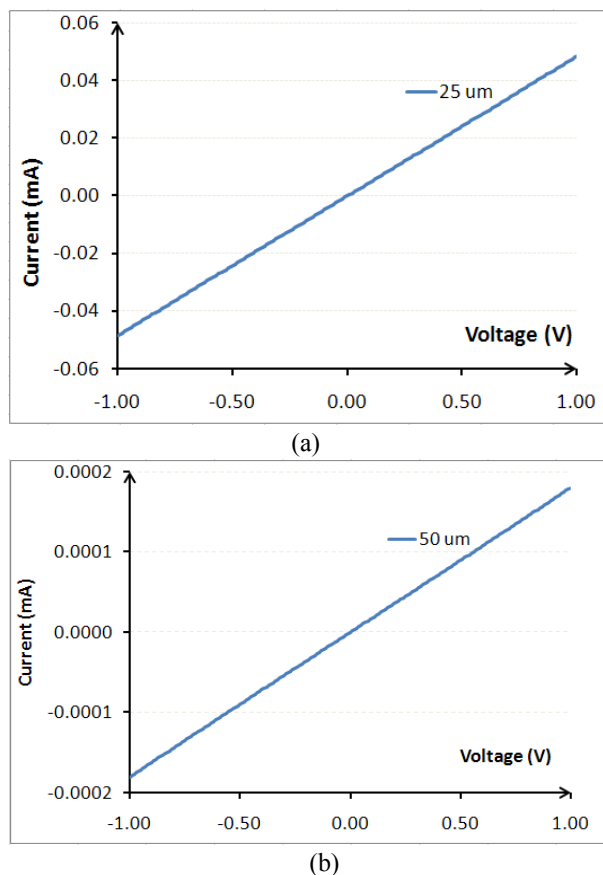


Figure 7. IV curves for (a) 25 μm and (b) 50 μm Au gap

By observing the values of the current in Figure 7 (a) and (b), we conclude that the TLM method cannot be used to extract the contact resistance and distinguish it from the series resistance, since the current does not scale with the channel length. This is most likely due to variations in morphology at the micrometer scale, and the possible existence of micrometer size domains. That explains why the current is so much larger for the 25 μm device compared to the 50 μm device where the disorder among the crystalline phases is much higher.

The important conclusion to report from this experiment is that the channel is quite conductive for a 25 μm channel length (about 25 K Ω total resistance), despite the lack of gate bias, the roughness of the paper, and being exposed to oxygen and light for a long period of time. Possible ways to improve the quality of the semiconductor are optimizing the time and temperature of curing, increasing the thickness of the film by printing more layers, improving the quality of the solution in order to have a more uniform jetting and changing the printer settings.

To study the transformation of pentacene precursor to pentacene, Differential Scanning Calorimetry (Q2000 DSC TA Instruments) was conducted at a ramp rate of 5 $^{\circ}\text{C}/\text{min}$ up

to 300 $^{\circ}\text{C}$. DSC results in Figure 8(a) show a strong exothermic peak with an onset temperature of 171.48 $^{\circ}\text{C}$. This peak is most likely the result of the pentacene precursor conversion. The onset temperature obtained from DSC was significantly higher than initially expected. Future experiments should attempt conversion at temperatures >180 $^{\circ}\text{C}$, under inert atmosphere. DSC of the transformed pentacene sample showed no exothermic peak that would indicate further crystallization following transformation. However, it is possible that recrystallization occurs in parallel with the pentacene conversion. The endothermic peak in Figure 8(b) at 240 $^{\circ}\text{C}$ is likely the result of the crystalline melting. The sharp peak is indicative of the transformed pentacene highly crystalline nature.

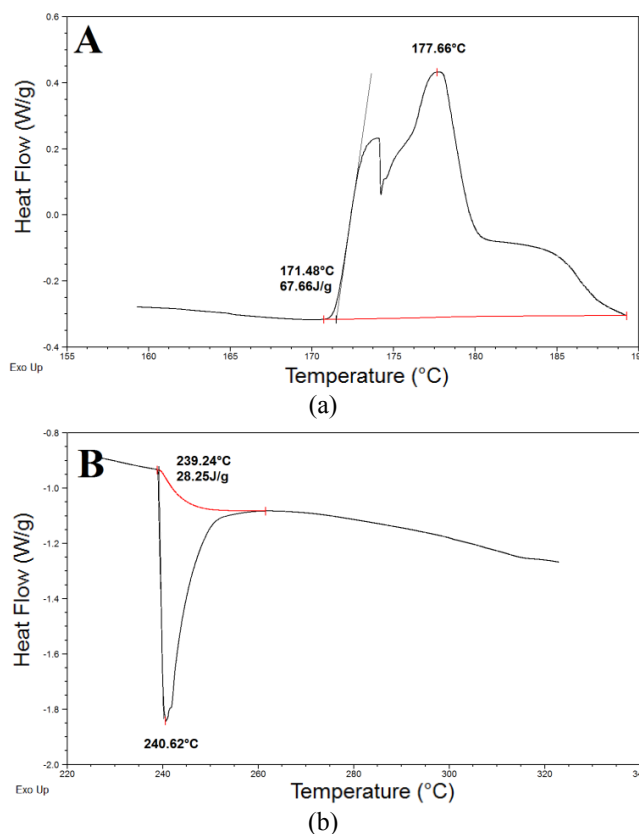


Figure 8. DSC of (a) pentacene conversion (b) crystalline melting

Further confirmation of the pentacene conversion was confirmed with Fourier Transform Infrared Spectroscopy (FT-IR: Nicolet, Magna IR 560) in Figure 8. Comparison of the fingerprint region of our transformed pentacene to literature confirmed characteristic absorption peaks at 906 cm^{-1} and 732 cm^{-1} [17].

Conclusions

The work presented in this paper identified the right organic materials and showed the printability of all the building blocks of an organic field-effect transistor (OTFT). For the semiconductor, a highly soluble pentacene precursor, 13,6-N-Sulfinylacetamidopentacene, was proposed. Anisole, a high boiling point solvent was chosen to insure proper jetting of the

solution. For the gate dielectric, two solutions were proposed: (i) using the paper itself as an insulator and print a bottom gate device on both sides of double sided glossy paper, (ii) a pentacene impurity, of 6,13-pentacenequinone (PQ), in a top gate configuration, may improve the device mobility by reducing the scattering sites at the semiconductor-dielectric interface. For the electrodes, the popular printable nanoparticle based silver ink will have to be either modified to match its work function with the pentacene's highest occupied molecular orbital (HOMO) level, or replaced with an alternate printable solution like Carbon Nanotubes (CNTs). Preliminary electrical testing of the pentacene film printed directly on paper showed good conduction properties for a 25 μm channel length. Further improvement of the pentacene film performance was proposed. This work established the foundation for the first fully inkjet printed OTFT on paper, as a fundamental building block of the sustainable electronics of the 21st century.

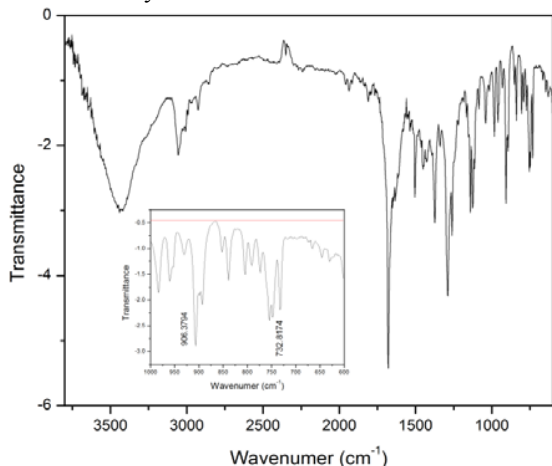


Figure 9. FT-IR of converted pentacene

Acknowledgments

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