#### <u>Preprint in press</u> <u>Accepted to be published in Advanced Electronic Materials</u>

#### **Article type: Full Paper**

# Fully High-Speed Gravure Printed, Low-Variability, High-Performance Organic Polymer Transistors with Sub-5V Operation

Gerd Grau and Vivek Subramanian\*

G. Grau and Prof. V. Subramanian Department of Electrical Engineering and Computer Sciences University of California, Berkeley Berkeley, CA 94720-1770 Email: <u>viveks@eecs.berkeley.edu</u>

Keywords: Organic thin film transistors (OTFT), gravure printing, printed electronics, high-speed printing, low variability

Printed transistors will be a key component in low-cost, large area, flexible printed systems such as flexible displays, sensor networks or RFID tags. In any such application, these printed organic thin film transistors (OTFTs) will have to operate at low voltages, exhibit good uniformity and deliver relatively high performance by using scaled source and drain electrodes. In addition, devices need to be printed at high speeds to fully harness the potential of low-cost fabrication that printed electronics promises. Gravure printing is a particularly promising technique because it combines high resolution in the sub-10µm regime with high printing speed on the order of 1m/s. Here, for the first time, fully gravure printed OTFTs are demonstrated that use highly scaled source and drain electrodes with linewidth and spacing of 5µm. All layers are printed at 1m/s. An amorphous polymer semiconductor is used to achieve 1

good uniformity. By patterning the semiconductor and scaling the dielectric, good off-state performance and sub-5V operation is achieved thus providing a promising path for the realization of functional printed systems.

#### 1. Introduction

Printed electronics is an emerging technology that holds great promise. Printing offers many advantages over classical microfabrication. One of its main advantages is the potentially low cost fabrication that it delivers. The additive nature of printing means that no subtractive etching, photolithography or vacuum processing steps are needed. Print speeds can be very high on the order of meters per second.<sup>[1]</sup> Both of these factors result in low-cost fabrication per unit area especially for large volume production. In addition, printed materials such as metal nanoparticles as well as organic semiconductors and dielectrics can be deposited and converted into their final form at very low temperatures that are compatible with low-cost, flexible plastic and paper substrates.<sup>[2,3]</sup> The most likely applications of printed electronics on such low-cost, flexible substrates would be cheap, portable, large volume, disposable systems such as RFID tags, flexible displays or sensors on food packaging.<sup>[4–7]</sup> Many such systems would require printed organic thin film transistors (OTFTs) for tasks such as signal amplification, pixel selection in an active matrix or simple logic. In order to fully enable such applications, printed transistors need to fulfill a number of requirements. These OTFTs need to deliver relatively high performance; performance can be improved by exploiting innovations in both materials and printing resolution. Furthermore, the supply voltage will 2

likely be limited. In many such systems power will be supplied by a printed battery or a printed solar cell, placing constraints on available voltage. Additionally, in order to fully benefit from the promise of high-throughput, low-cost fabrication, all transistor layers need to be printed at high printing speeds. Finally, device-to-device variation needs to be small to realize any realistic circuit.

In the past, many reports have demonstrated tremendous progress in one or more of these areas. Many reports have shown that novel organic semiconductor materials can boost performance.<sup>[8–10]</sup> Performance can also be enhanced by using careful crystallization techniques.<sup>[11–14]</sup> It has been shown that thin gate dielectrics can be used to reduce the operating voltage significantly.<sup>[15–17]</sup> However, much of this work was performed with idealized systems that are not compatible with high volume printing, for example using silicon substrates, evaporated contacts or spin coating. In addition, crystallized semiconductors typically exhibit variability due to the random placement of grain boundaries. There has been work to improve uniformity and produce fully solution-processed<sup>[18]</sup> or printed devices.<sup>[19]</sup> However, these works did not employ high-speed printing techniques that can run at speeds on the order of meters per second and the feature size was limited to tens of micrometers. Recently, transistors have been fabricated with highly scaled feature sizes below 5µm that have been printed using reverse offset<sup>[20]</sup> and gravure printing<sup>[21]</sup>; however, some of the layers were still fabricated with lower speed techniques.

Here, we print OTFTs where every layer is printed by gravure (see **Figure 1** (a) for an illustration of the gravure process) with a high print speed of 1m/s including highly scaled source and drain lines with feature sizes on the order of 5µm. By scaling the gate dielectric, the operating voltage is reduced to less than 5V. An amorphous polymer semiconductor is used to reduce variability in comparison with polycrystalline small-molecule semiconductors. Thus, we are, for the first time, able to realize highly-scaled state-of-the-art high performance organic transistors delivering good performance, low-voltage operation, all realized using a fabrication process based on high-speed gravure printing of all layers.

In order to achieve this excellent performance, every layer needs to be studied carefully. Each layer has its own specific challenge when implemented by gravure. The source and drain electrodes require excellent pattern fidelity in order to achieve high-resolution printing for high-frequency device operation. Here, we show how highly-scaled 5µm features can be printed whilst simultaneously achieving high printing yield. The dielectric is the most important layer to reduce operation voltage. By reducing the dielectric thickness, the gate field and thus gate control is increased. We employ a leveling step to improve thickness uniformity for thin dielectric films. Printing of the semiconductor is challenging because it requires printing-based patterning of a thin uniform layer. The effect of ink viscosity on this printing is explored and optimized. Finally, the gate electrode and device structure are

optimized to facilitate gravure-printed device formation. For gravure printing, alignment accuracy currently lags behind feature size, which means alignment of the gate electrode to the source and drain electrodes is very challenging. Alignment accuracy is reduced both by tool limitations, which will be addressed in future generation tools, as well as by more fundamental issues with flexible substrates such as stretching or dimensional changes during heating steps. Addressing these challenges in the future would be an important step forward for the gravure printing of multi-layer devices. In the meantime, we employ a fully overlapped gate structure with a large gate electrode. Due to the large size of the gate relative to the channel and source-drain dimensions, the structure becomes misalignment tolerant.<sup>[22]</sup> Thus, gate pattern size is not very critical. The main challenge with the gate is to choose an ink that sufficiently wets the dielectric and whose solvent does not interact with the dielectric. See Figure 1 (b) for the device structure and the fabrication process.

#### 2. Source drain printing

Downscaling of the source and drain electrodes and their spacing is crucial to achieve highperformance TFT operation. Gravure printing has been demonstrated to print high resolution features below 10µm at high print speeds on the order of 1m/s.<sup>[21,23]</sup> In order to achieve good AC performance, the fully overlapped gate architecture requires not only a highly scaled channel length but also highly scaled electrodes to minimize overlap capacitance. Here, we print electrodes whose width is on the same order as the channel length. The electrode pattern on the printing plate is a string of individual cells. The print speed and ink viscosity need to be 5

controlled to be able to print from these highly scaled cells. Capillary number (Ca) is a dimensionless quantity that determines the outcome of the individual sub-processes during the gravure process.<sup>[23]</sup> Ca is defined as the product of print speed and ink viscosity divided by ink surface tension. At small values of Ca, too much ink is dragged out of cells during the doctor blade wiping process reducing the amount of ink that is printed onto the substrate. At large values of Ca, ink filling of the cells is inhibited and the printed ink amount is also reduced. Thus, an optimum point exists where both drag-out is minimized and cells are still fully filled with ink. This optimum point typically lies between a capillary number of 1 and 5.<sup>[24]</sup> Another important consideration is the spreading of the ink on the substrate after transfer. Ink needs to have a viscosity that is high enough to prevent uncontrolled spreading whilst still filling in the gaps between individual cells. A viscosity on the order of 100cP has proven to be optimal.<sup>[25]</sup> In order to meet these requirements as well as print at 1m/s, we chose an ink viscosity of 86cP, which results in a capillary number of 3.4. Line width can be adjusted by varying the cell size. The printed line width is linearly related to line width on the printing plate. Ink spreading on the plastic substrate slightly increases the printed line width (see Figure S1). Similarly, the printed channel length is reduced by ink spreading from the adjacent lines (see Figure S2).

At such highly-scaled channel lengths below  $5\mu m$ , the limiting factor on yield is the merging together of closely spaced source and drain electrodes. **Figure 2** (a) shows the relation

between channel length and printing yield. Perfect yield can be achieved down to about 10µm channel length and vield is close to 100% down to 5um channel length. Shorter channel lengths can still be printed but yield drops off very quickly. A major factor to achieve this excellent yield is the doctor blade. The doctor blade is a very important component of the gravure process. Its main function is to wipe off excess ink from the land areas of the roll and on top of the cells after the ink has filled the cells. Ideally, land areas are free of ink and cells are fully filled with ink after the wiping process. However, in reality there are two important non-idealities in the wiping process. A uniform, thin lubrication residue film is left by the finite gap that always exists between the doctor blade and the printing plate.<sup>[26]</sup> In addition, the drag-out effect occurs when the blade passes over cells. Ink wicks up the backside of the blade, is lost from the cell and is subsequently deposited behind the cell as a characteristic drag-out tail.<sup>[23]</sup> Here, lines are printed parallel to the printing direction, which minimizes the effect of these tails; however, ink can still somewhat spread sideways on the blade as it gets dragged out of the cells, which can lead to the merging of adjacent lines. Ideally, both wiping non-idealities occur uniformly across the print. However, doctor blades typically have local defects whose density gets worse during printing due to doctor blade wear. In the worst case, these defects can cause the printing of large streaks that run throughout the print. Even without such catastrophic streaks, doctor blade defects and wear affect yield dramatically for highly scaled features. Figure 2 (b) shows how yield changes throughout a print for different doctor blade tip thicknesses (see Figure 2 (c) for cross-sectional micrographs of different

blade tips). A thin 60µm tip shows dramatic degradation in yield as the print progresses because it is very susceptible to wear. A 75µm tip is far more robust. Yield even increases slightly after the beginning of the print, possibly because initial defects are polished away. However, increasing the tip thickness too much leads to decreased print quality and yield as evidenced by the 95µm tip. Larger tips develop a smaller pressure at the tip leading to increased lubrication residue and allow more time for drag-out to occur. A 75µm tip was thus used to fabricate devices.

#### 3. Semiconductor printing

The semiconductor material is crucial in determining the performance of a transistor. Here, we employ lisicon® SP400 provided by EMD Performance Materials Corp. This p-type semiconductor is a high-performance amorphous polymer. Its mobility is on-par with state-of-the-art small molecule semiconductors in fully printed short-channel OTFTs. The amorphous nature of the material reduces processing complexity and variability because there is no need for a crystallization step, and device to device uniformity is improved due to the elimination of grain boundary-induced variation as a performance-determining parameter. In addition, patterning and control over the rheology is significantly improved by the fact that lisicon® SP400 is a polymer rather than a small molecule. Patterning of the semiconductor layer is, in practice, imperative to realize functional organic semiconductor-based circuits. When the semiconductor is patterned, leakage paths are removed that would otherwise lead to excessive device off-current and cross-talk between neighboring devices. The pattern dimensions for the 8

semiconductor are much larger than for the source and drain electrodes, typically on the order of tens to hundreds of micrometers. However, patterning of the semiconductor is more challenging because low viscosity inks are used to achieve thin films. The use of thin films is desirable to obtain good device electrostatic integrity, resulting in improved off-state behavior. Lowering the polymer concentration in the ink decreases both dry film thickness and ink viscosity. Figure 3 (a) shows how the pattern fidelity changes with different ink viscosities. As the viscosity is reduced, pattern fidelity becomes worse due to increased ink spreading on the substrate. Down to 24cP individual device patterns are still distinct. At 9cP the ink spreads so much that no distinct features can be made out anymore. At 9cP the thickness of the printed film also becomes too thin to be measured accurately on a flexible plastic substrate. The other ink viscosities show the expected trend of decreased thickness with decreased ink viscosity (see Figure 3 (b)). Higher viscosity patterns also exhibit reduced levels of coffee ring i.e. the accumulation of material at the edges of features where the solvent dries faster than in the center. Thus, from a patterning perspective, higher viscosity semiconductor inks are desirable. However, a thin semiconductor layer is required for optimal device performance. Mobility drops as the semiconductor ink viscosity is increased past 24cP (see Figure 4 (a)). At 9cP the semiconductor film is too thin to carry any substantial current. At higher viscosities contact resistance limits device operation (see Figure 4 (b)). Since the device structure is top-gate bottom-contact, holes need to be conducted from the electrodes through

the thickness of the semiconductor to the channel. This leads to increased contact resistance for thicker semiconductor films. Thus, a 24cP ink was used for device fabrication.

#### 4. Dielectric scaling

The gate dielectric is crucial in ensuring good electrostatic control over the channel. Here, we use lisicon® D320, a polymer dielectric provided by EMD Performance Materials Corp., which has been designed to match with the semiconductor lisicon® SP400. The semiconductor-dielectric interface is optimized to ensure a low trap concentration, enabling the realization of devices with high mobility and low subthreshold swing. In addition, the semiconductor is compatible with the dielectric solvent (decane). It is also important for the dielectric to have a high enough surface energy such that the subsequent gate ink does not dewet, which is a problem for fluorinated gate dielectrics. In order to achieve low-voltage operation, the gate dielectric needs to be scaled down in thickness to increase the gate field and improve gate control over the channel. Here, we studied a number of different dielectric thicknesses. Thickness was varied by dilution of the dielectric ink. As the dielectric thickness is scaled, off-state performance improves significantly (see Figure 5). For a 120nm thick dielectric, the magnitude of the threshold voltage decreases to approximately -1V and swing drops below 500mV/decade. In order to achieve such thickness scaling, a very uniform dielectric needs to be printed. Gravure printing often leads to non-uniform films due to fluid instabilities as well as the discrete nature of the gravure cells that requires ink to spread in between cells.<sup>[27]</sup> Here, we employ a leveling step in a solvent atmosphere to improve the 10

uniformity of the dielectric thickness and dielectric yield significantly (see Figure S3). However, dielectric yield still needs to be improved further (see Figure S4). Further improvements might be possible by modifying the gate ink to improve solvent compatibility, and by improving the cleanliness of the processing environment. Improvements in the surface roughness of the underlying source and drain electrodes (currently RMS roughness 15.3nm) might also increase dielectric yield (see Figure S 5). In any case, the current process enables the fabrication of functioning devices with a 120nm thick gravure printed dielectric. **Figure 6** shows representative device characteristics for such devices. The operation voltage is below 5V, which is very low for organic transistors, especially when fully printed. On-off ratios exceeding 10<sup>5</sup> are achieved at these low voltages. The transition frequency, i.e. the frequency at which current gain becomes unity, was measured for these low-voltage transistors. Transistors were tested in an inverter configuration with an external load resistor. A transition frequency of 96kHz was achieved. To the best of our knowledge this is the highest transition frequency reported to date for fully high-speed printed transistors on flexible substrates operating at sub-5V voltages.

#### 5. Comparison with small molecule semiconductor

One reason for choosing a polymer semiconductor is its better printability compared with small molecule semiconductors. This facilitates the printing of patterned semiconductor pads. In addition, the polymer used here is amorphous, which allows for achievement of very good device-to-device uniformity. In contrast, the performance of small molecule polycrystalline 11

organic semiconductors depends very strongly on the grain size and the location of grain boundaries. Due to the random nature of the crystallization process, devices with small molecule semiconductors tend to be more variable than devices with amorphous semiconductors. Furthermore, polycrystalline semiconductors have larger surface roughness due to grain boundaries that can be problematic for the yield of the dielectric deposited on top. Here, we compare our amorphous polymer TFTs with devices fabricated using a state-of-theart polycrystalline small molecule semiconductor (Lisicon® S1200) supplied by EMD Performance Materials Corp. These small molecule devices were fabricated with a very similar process except the small molecule semiconductor was polycrystalline and not patterned, the dielectric was 200nm thick and the gate was patterned by inkjet printing.<sup>[22]</sup> Figure 7 shows the difference in electrical performance between the polymer and the small molecule devices. The improved uniformity of the polymer devices both in the on- and the off-state is clearly visible. Small molecule devices typically exhibit better on-state performance due to their crystallinity. This can be observed in the saturation mobility. Linear mobility is similar for the polymer and the small molecule devices because of the excellent contact resistance achieved here. Off-state performance is improved significantly by using the polymer semiconductor because of the thinner dielectric and the patterning of the semiconductor. This allows the polymer devices to be operated at significantly lower voltages.

#### 6. Discussion

When designing and fabricating fully-printed devices, it is imperative to consider the device as a whole, with a particular focus on the layer interactions. For example, AC performance is boosted by scaling down the width of the source-drain electrodes and the channel length. This creates a need to scale down the thicknesses of the other layers to maintain good device electrostatic control. Due to the shorter channel length, contact resistance becomes more dominant relative to the reduced channel resistance. Since holes are conducted through the thickness of the semiconductor layer, the semiconductor thickness needs to be scaled down as the source and drain dimensions are scaled down; this also facilitates improved swing by improving gate control over the entire channel film. Quantitatively, on-current scales linearly with the reciprocal of the channel length (1/L) i.e. channel resistance scales linearly with channel length. Contact resistance due to conduction through the thickness of the semiconductor film scales linearly with the thickness of the semiconductor film. Thus, as channel length is scaled down, semiconductor film thickness needs to be scaled down by the same factor to maintain the same impact of contact resistance due to conduction through the thickness of the semiconductor. Similarly, shorter channels result in a need for a thinner gate dielectric. As the source and drain electrodes are brought closer together, the effect of the drain field on the channel region increases, which will degrade off-state performance and increase leakage current. To counter this increased drain field, the gate field needs to be increased accordingly, which can be achieved by scaling down the thickness of the gate dielectric. If the dielectric thickness is scaled down by the same factor as the channel length, 13

the operating voltage can also be scaled down by this factor. In this case, all the electric fields have stayed constant and the electrostatic integrity of the device has been maintained during scaling. These considerations are well known from classical MOSFET scaling. Here, we apply these principles, for the first time, to fully high-speed printed OTFTs. By printing every layer with gravure at 1m/s, we demonstrate that scaling of fully high-speed printed devices is possible, and show that high performance organic transistors can indeed be delivered using high-speed printing processes. This is a major step towards the manufacturability of printed OTFTs with high-throughput techniques to fully benefit from the promise of low-cost fabrication.

#### 7. Conclusions

Fully gravure printed organic thin-film transistors are demonstrated. Every transistor layer is high-speed printed at 1m/s. Highly-scaled source drain lines are printed with high yield down to 5µm linewidth and spacing. An amorphous polymer semiconductor is used for its good printability and uniformity. By patterning the semiconductor and scaling the dielectric, good off-state performance is achieved allowing operation below 5V. This is a significant step towards the realization of fully high-speed printed, low-cost, high-performance electronic systems.

#### 8. Experimental

#### 8.1. Materials

Devices were fabricated on planarized polyethylene naphthalate (PEN) substrates (PQA1) provided by DuPont Teijin Films. The source and drain electrodes were printed using a silver nanoparticle ink (NPS) purchased from Harima Chemicals Group. The viscosity of this ink was adjusted to 86cP by dilution with its solvent AF5. The active organic materials were provided by EMD Performance Materials Corp. (an affiliate of Merck KGaA, Darmstadt, Germany): lisicon® M001 (surface treatment for the source and drain electrodes, used as received), lisicon® SP400 (amorphous polymer semiconductor, diluted with mesitylene and 1-methyl naphthalene) and lisicon® D320 (gate dielectric polymer ink, diluted with decane). The gate electrode was printed using another silver nanoparticle ink (Silverjet DGP 40LT-15C) as received from Advanced Nano Products (ANP). Three different types of doctor blades with different tip thicknesses (60µm, 75µm, 95µm) were used for gravure printing as supplied by Max Daetwyler Corporation.

#### 8.2. Fabrication processes and characterization

Top-gate bottom-contact OTFTs were fabricated. All layers were printed using gravure printing. All layers were printed at the maximum print speed achievable on our laboratory scale printer: 1m/s. PEN substrates were laser cut and cleaned by sonication in acetone and isopropanol. Substrates were treated with a 30 seconds, 50W air plasma before printing of the source and drain electrodes. The source and drain electrodes were printed using inverse direct

gravure. Silicon printing plates were fabricated using conventional microfabrication.<sup>[23]</sup> The cells that make up the pattern are etched into the silicon using KOH to achieve an inverted pyramid cell shape. The cell width was varied from 3 to 7.5µm whilst the cell gap was kept constant at 0.1 times the cell width. After printing of the source and drain electrodes, the silver ink was sintered at 220°C for 2 hours with a slow ramp rate of 3°C/min to improve electrode adhesion to the substrate. Before printing of the semiconductor, a two-step surface treatment was applied to improve contact resistance.<sup>[21]</sup> First, the source and drain electrodes were exposed to a mild 10W RF plasma in air for 30 seconds. Then, samples were dried at 100°C for 5 minutes to remove any residual moisture before applying a self-assembled monolayer (SAM). This drying step is critical to achieve good adhesion of the source and drain electrodes to the substrate during the subsequent semiconductor printing step. Lisicon® M001 was applied by drop casting. After drying, the samples were rinsed with isopropyl alcohol, dried again and dried at 100°C for 1 minute. This surface treatment process could easily be implemented with a simple roll-to-roll compatible technique such as blade coating and was thus not implemented with gravure. The semiconductor was gravure printed using conventional direct gravure with a metal roll fabricated by electromechanical engraving purchased from RotaDyne. The semiconductor was patterned by using rectangular cell patterns. The gate dielectric layer was blanket printed using a roll purchased from IGT Testing Systems (402.101, 45µm cell depth). In order to improve thickness uniformity, the printed dielectric film was allowed to level in an enclosed environment for 1 hour before

drying at 100°C for 5 minutes. Before printing of the gate, the gate dielectric was treated with a mild air plasma (25W, 10 seconds) to increase the surface energy. The gate electrode was patterned by using the same electromechanically engraved roll purchased from RotaDyne. The gate was sintered for 5 minutes at 100°C with a ramp rate of 2°C/minute. Transistor characteristics were measured using an Agilent 4156C semiconductor parameter analyzer in a nitrogen atmosphere. All fabrication steps were performed in air. Contact resistance was extracted using the transmission line method. The transition frequency was measured by connecting an external resistor to the TFT and applying an AC signal to the gate with an HP 33120A function generator. The output was measured using a Tektronix TDS 3014 oscilloscope.

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

#### Acknowledgements

We acknowledge EMD Performance Materials Corp. (an affiliate of Merck KGaA, Darmstadt, Germany) for providing the active organic materials, Dupont Teijin Films for providing the PEN plastic substrates and Max Daetwyler Corporation for providing the doctor blades. This work is funded in part by EMD Performance Materials Corp.

- V. Subramanian, J. Cen, A. de la Fuente Vornbrock, G. Grau, H. Kang, R. Kitsomboonloha, D. Soltman, H.-Y. Tseng, *Proc. IEEE* 2015, 103, 567.
- [2] D. Tobjörk, R. Österbacka, Adv. Mater. 2011, 23, 1935.
- [3] G. Grau, R. Kitsomboonloha, S. L. Swisher, H. Kang, V. Subramanian, *Adv. Funct. Mater.* **2014**, *24*, 5067.
- [4] Namsoo Lim, Jaeyoung Kim, Soojin Lee, Namyoung Kim, Gyoujin Cho, *Adv. Packag. IEEE Trans. On* **2009**, *32*, 72.
- [5] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, *Nat Mater* **2009**, *8*, 494.
- [6] J. B. Chang, V. Liu, V. Subramanian, K. Sivula, C. Luscombe, A. Murphy, J. Liu, J. M. J. Fréchet, J. Appl. Phys. 2006, 100, 014506.
- [7] T. Someya, Y. Kato, T. Sekitani, S. Iba, Y. Noguchi, Y. Murase, H. Kawaguchi, T. Sakurai, *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 12321.
- [8] J. E. Anthony, D. L. Eaton, S. R. Parkin, Org. Lett. 2002, 4, 15.
- [9] R. Hamilton, J. Smith, S. Ogier, M. Heeney, J. E. Anthony, I. McCulloch, J. Veres, D. D. C. Bradley, T. D. Anthopoulos, *Adv. Mater.* 2009, 21, 1166.
- [10] J. Smith, R. Hamilton, I. McCulloch, N. Stingelin-Stutzmann, M. Heeney, D. D. C. Bradley, T. D. Anthopoulos, J. Mater. Chem. 2010, 20, 2562.
- [11] H. Minemawari, T. Yamada, H. Matsui, J. Tsutsumi, S. Haas, R. Chiba, R. Kumai, T. Hasegawa, *Nature* 2011, 475, 364.
- [12] Y. Yuan, G. Giri, A. L. Ayzner, A. P. Zoombelt, S. C. B. Mannsfeld, J. Chen, D. Nordlund, M. F. Toney, J. Huang, Z. Bao, *Nat. Commun.* 2014, 5, DOI 10.1038/ncomms4005.
- [13] G. Giri, E. Miller, Z. Bao, J. Mater. Res. 2014, 29, 2615.
- [14] G. Grau, R. Kitsomboonloha, H. Kang, V. Subramanian, Org. Electron. 2015, 20, 150.
- [15] M.-H. Yoon, H. Yan, A. Facchetti, T. J. Marks, J. Am. Chem. Soc. 2005, 127, 10388.
- [16] Y. D. Park, D. H. Kim, Y. Jang, M. Hwang, J. A. Lim, K. Cho, Appl. Phys. Lett. 2005, 87, 243509.
- [17] S. Lai, P. Cosseddu, G. C. Gazzadi, M. Barbaro, A. Bonfiglio, Org. Electron. 2013, 14, 754.
- [18] K. Fukuda, Y. Takeda, M. Mizukami, D. Kumaki, S. Tokito, *Sci. Rep.* 2014, *4*, DOI 10.1038/srep03947.
- [19] A. Pierre, M. Sadeghi, M. M. Payne, A. Facchetti, J. E. Anthony, A. C. Arias, Adv. Mater. 2014, 26, 5722.
- [20] K. Fukuda, Y. Yoshimura, T. Okamoto, Y. Takeda, D. Kumaki, Y. Katayama, S. Tokito, *Adv. Electron. Mater.* **2015**, *1*, n/a.
- [21] H. Kang, R. Kitsomboonloha, K. Ulmer, L. Stecker, G. Grau, J. Jang, V. Subramanian, *Org. Electron.* **2014**, *15*, 3639.
- [22] R. Kitsomboonloha, H. Kang, G. Grau, W. J. Scheideler, V. Subramanian, Adv. Electron. Mater. 2015, DOI 10.1002/aelm.201500155.

- [23] R. Kitsomboonloha, S. J. S. Morris, X. Rong, V. Subramanian, *Langmuir* 2012, 28, 16711.
- [24] G. Grau, R. Kitsomboonloha, V. Subramanian, in *Proc SPIE 9568*, San Diego, **2015**, p. 95680M.
- [25] G. Grau, W. J. Scheideler, V. Subramanian, in *Proc SPIE 9569*, San Diego, 2015, p. 95690B–1.
- [26] R. Kitsomboonloha, V. Subramanian, Langmuir 2014, 30, 3612.
- [27] G. Hernandez-Sosa, N. Bornemann, I. Ringle, M. Agari, E. Dörsam, N. Mechau, U. Lemmer, *Adv. Funct. Mater.* **2013**, *23*, 3164.





**Figure 1.** (a) Overview of the gravure printing process. Patterns are defined by recessed cells that are engraved into a roll. The cells are filled with ink from an ink reservoir. Excess ink is wiped off the roll surface using a doctor blade. Ink is transferred from the roll to a substrate such as plastic or paper. Ink spreads on the substrate to fill in the gaps between individual cells. (b) Overview of fabrication process and device structure. (i) Highly-scaled silver electrodes are gravure printed on cleaned PEN plastic substrates. (ii) After a self-assembled monolayer treatment, the polymer semiconductor is patterned using gravure printing. (iii) The dielectric is blanket printed using gravure. (iv) The silver gate electrode is patterned by gravure printing. All printing steps are performed at 1m/s in air.



**Figure 2.** Printing yield of source-drain patterns. (a) Yield is close to 100% for channel lengths above 5µm. Below 5µm, the number of merged lines increases significantly. (b) Yield depends significantly on the thickness of the doctor blade tip. 60µm blades show significant degradation during prints due to wear. 95µm blades show decreased yield due to insufficient pressure. 75µm blades exhibit good yield with reduced wear. (c) Cross-sectional micrographs showing the tip of the doctor blade for three different blade tip thicknesses, which is measured at the very tip of the blade.

(a)

9cP:



24cP:



36cP:



130cP:



175cP:



**—** 30µm



**Figure 3.** Semiconductor pattern definition for different ink viscosities. (a) Optical micrographs showing printed semiconductor patterns on top of printed source and drain lines. Lateral pattern definition improves with increased viscosity. 9cP spreads uncontrollably. 24cP and above exhibits defined patterns. (b) Pattern thickness increases and relative coffee ring height decreases with increasing viscosity.



**Figure 4.** Effect of semiconductor viscosity on electrical performance. (a) Linear mobility increases with decreasing viscosity until the semiconductor film becomes too thin to conduct significant current. (b) Thinner semiconductor films printed with lower viscosity inks lead to improved contact resistance in a top-gate bottom-contact device structure where current is conducted through the semiconductor thickness.



**Figure 5.** Off-state performance improves significantly with thinner gate dielectrics due to better gate control.

(a)





**Figure 6.** Representative transfer and output characteristics exhibiting low-voltage operation with excellent off-state performance.





**Figure 7.** Comparison of amorphous polymer and polycrystalline small molecule semiconductor devices. Polymer devices exhibit better uniformity. (a) Small molecule devices exhibit slightly higher saturation mobility. (b) Linear mobility is comparable due to the excellent contact resistance achieved here. (c) and (d) Both swing and threshold voltage are significantly better for the polymer devices due to a thinner gate dielectric and patterning of the semiconductor.

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**Fully high-speed printed OTFTs are demonstrated.** All layers are gravure printed at 1m/s with source-drain and channel dimensions of 5µm. Good uniformity is achieved by employing an amorphous polymer semiconductor. By patterning the semiconductor and scaling the dielectric, low-voltage operation below 5V is achieved. This is a promising result for the realization of low-cost, large area, flexible printed systems.

Keyword: Organic thin film transistors (OTFT), gravure printing, printed electronics, highspeed printing, low variability

Gerd Grau and Vivek Subramanian\*

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#### **Supporting Information**

Fully High-Speed Gravure Printed, Low-Variability, High-Performance Organic Polymer Transistors with Sub-5V Operation

Gerd Grau and Vivek Subramanian\*



**Figure S1.** Printed linewidth is linearly related to line width (=cell width) on the printing plate. Printed line width is slightly enlarged by ink spreading on the substrate.



**Figure S2.** Printed channel length is linearly related to channel length on the printing plate. Channel length is reduced by ink spreading on the substrate.



**Figure S3.** Dielectric thickness uniformity and yield are improved significantly by allowing the film to level in a solvent atmosphere before drying, to remove any non-uniformities after gravure printing. Data for 300nm thick film.



**Figure S4.** The dielectric yield of gravure printed dielectric is perfect down to a thickness of 300nm. Below this thickness, further improvements in yield are required.



**Figure S 5.** Height profile of source and drain lines. The average RMS surface roughness is 15.3nm. Improvements in source and drain surface roughness might improve dielectric yield.