ALL-PRINTED FLEXIBLE ORGANIC THIN FILM TRANSISTORS: CURRENT STATUS AND OUTLOOK FOR THE FUTURE

V. Subramanian[1], J. M. J. Fréchet[2], P. C. Chang[1], D. C. Huang[1], J. B. Lee[1], F. Liao[1], B. A. Mattis[1], S. Molesa[1], A. R. Murphy[2], D. R. Redinger[1], S. K. Volkman[1]
[1]Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, CA 94720-1770
[2]Department of Chemistry, University of California, Berkeley, CA 94720-1460

Printed organic electronics is promising for realizing low-cost flexible displays and RFID tags. We describe the state of the art in printed organic electronics, focusing on advanced materials currently being studied to realize devices with enhanced performance, including soluble oligomer semiconductor precursors, printable self-assembled monolayer dielectrics, and printable high-K dielectric precursors. These materials should enable the realization of devices with low operating voltages and carrier mobilities sufficiently high for the demonstration of high-quality displays and RFID tags on plastic.

INTRODUCTION

Recently, there has been great interest in organic devices, driven by their applications in displays (1) and RFID tags (2). Organic electronics is promising due to its low fabrication cost and plastic compatibility. Organic devices are also amenable to solution processing. This is advantageous because (a) it eliminates conventional lithography since circuits may be printed (b) it eliminates vacuum processed steps such as PVD, CVD, and plasma etching (c) it is additive, thus reducing process complexity while simultaneously reducing waste-abatement costs, and (4) it enables the use of low-cost substrates in a reel-to-reel environment, thus reducing overall factory costs.

Over the last decade, performance of organic semiconductors has been improving steadily. Evaporated pentacene transistors with mobilities ~10cm^2/V-s have been reported (3). Solution-processed organic semiconductors have also progressed, with printed mobilities as high as 0.3cm^2/V-s (4) having been demonstrated. While advancement in organic semiconductor technology has been rapid, semiconductors alone do not facilitate the demonstration of fully-functional circuits; commensurate progress is also required in the associated conductor and dielectric technologies. In this paper, we shall review the current state of the art in printed semiconductor and dielectric technology.

OVERVIEW OF PRINTED ORGANIC ELECRONICS TECHNOLOGY

Printable organic semiconductors

Early work on printed organic devices focused on polymers, since these offer good solubility. In particular, mobilities approaching 0.1cm^2/V-s were obtained using poly(hexyl)thiophene (P3HT). Unfortunately, this material undergoes performance degradation upon air, moisture, and/or thermal exposure (5). Therefore, more recently,

efforts using polymer semiconductors have focused on materials offering better stability, such as F8T2 (6). In general, none of the polymer materials has achieved demonstrated carrier mobilities greater than 0.1cm^2/V-s, and generally, printed implementations of these materials have resulted in lower performance (10^{-3} to 10^{-2} cm^2/V-s).

To achieve the higher-performance requisite for many display and RFID applications, effort has been focused on oligomers, which form crystalline films offering improved stability and performance. Unfortunately, most oligomers are insoluble, and therefore not printable. To solve this problem, various groups have demonstrated oligomer precursors. These are soluble due to the presence of solubilizing groups in the precursor molecule. Upon deposition, the solubilizing groups are removed (typically through thermolysis), leaving an insoluble oligomer offering high-performance. Since the finished film is insoluble, it is possible to integrate the material into devices without concern for solvent-interactions from subsequent layers. Such precursors have been demonstrated for pentacene (7) with mobilities of 0.3cm^2/V-s having been realized in printed devices (4).

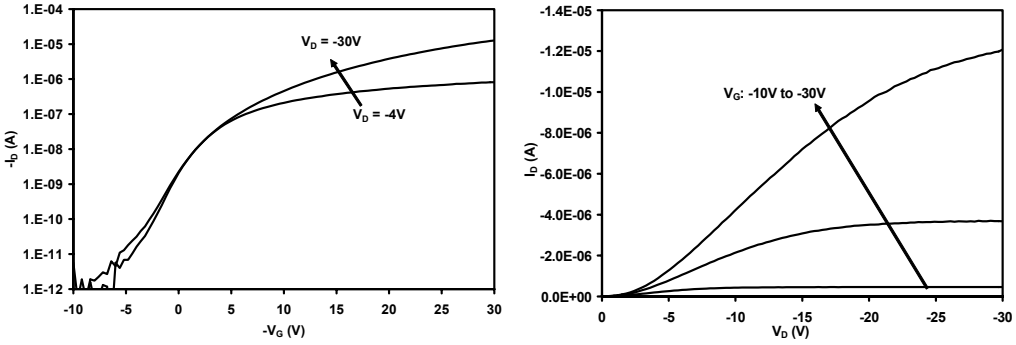

Figure 1: Characteristics of a printed pentacene transistor.

Similar results have also been obtained using oligothiophene precursors (8). Printed devices consisting of one monolayer of oligothiophene have been realized with good electrostatics and film crystallinity (9). This allows the realization of devices with field-effect mobilities > 0.1cm^2/V-s while offering excellent on-off ratios > 10^8. This is particularly important, since it minimized static power consumption.

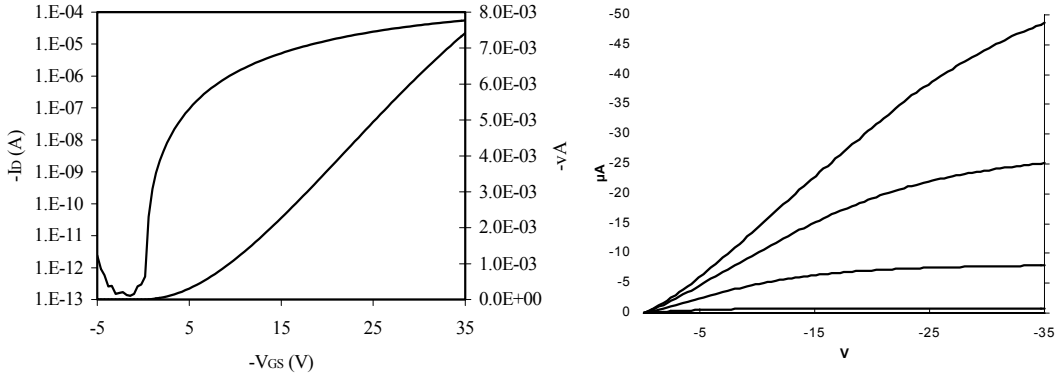

Figure 2: Characteristics of a printed single-monolayer oligothiophene transistor.

In general, progress in printable organic semiconductors is continuing, and it is likely that mobilities of ~1cm^2/V-s will be realized in the near future using such synthetic modifications as detailed above.

Printable dielectrics

Much of the early work on organic semiconductors was performed using an SiO_2 gate dielectric. This is not realistic for printed electronics. Fortunately, the highest performance transistors demonstrated to date have been realized using sputtered Al_2O_3 with an organic interlayer (3) and PVP (an organic dielectric) (10). Since organic semiconductors do not covalently bond to the dielectric, the choice of dielectrics is relaxed, though ordering effects become important (note that most OFETs are fabricated using an inverted staggered TFT structure, with the gate below the active layer). Here, we review trends in OFET dielectric materials and device issues.

Flexion Issues. Rlectronics on plastic will undergo substantial flexion during use and/or fabrication. Therefore, it is crucial that printed electronics be able to withstand flexion. In flexible electronics in general, the dielectric layer has been found to be the weak link in flexion studies. Even crystalline organic semiconductors such as pentacene show more flexion strength than their dielectric counterparts. For example, we have recently performed flexion studies on pentacene transistors formed on flexible fibers using either SiO_2 or PVP gate dielectrics (11). In both cases, irreversible damage to the transistor originated in gate dielectric cracking rather than in damage to the pentacene layer. This attests to the need for flexion studies as we develop novel dielectric materials.

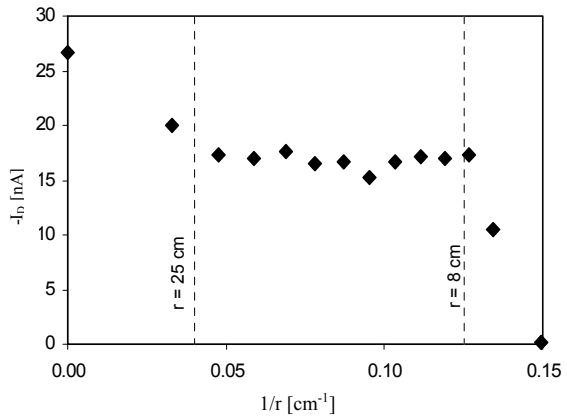

Figure 3: Flexion studies on pentacene transistors. The device death is accompanied by a dramatic increase in gate current, indicative of gate dielectric cracking.

Printing Issues. To achieve a fully additive process, it will be necessary to develop dielectrics that can be deposited by printing. Blanket deposition techniques are undesirable, since they will require the use of subsequent subtractive via formation steps. Printed dielectrics are problematic in their own right, however. To date, formation of thin dielectrics with good breakdown characteristics and low leakage by printing has been problematic. Many printing techniques, such as inkjet and screen printing, result in pixilation of the dielectric, with corresponding weak spots between pixels. Pixilation can only be avoided by either overlaying multiple layers (which results in thicker dielectrics)

(12) or allowing the droplets to flow together (which results in poor reproducibility and pattern integrity) (13). Some of these problems may be mitigated by using a non-pixilated printing scheme such as gravure or flexo. Unfortunately, these techniques have not been demonstrated to produce thin films of adequate quality to this point.

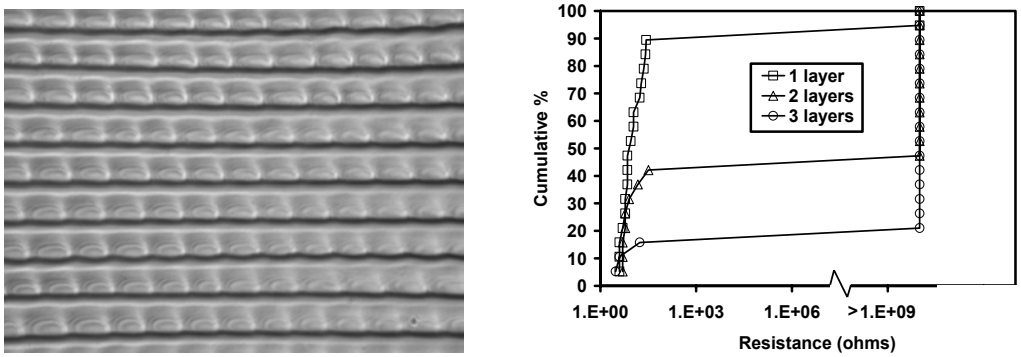

Figure 4: (a) Pixilation during printing, and (b) use of overlaid drops to improve yield.

Dielectric materials / film characteristics concerns. PVP is one of the most promising dielectrics for printed electronics. PVP delivers films with k~4, while offering good breakdown strength (1-5MV/cm). The high quality of this film is the result of the cross-linking used to produce a robust mechanical structure (10); material that isn't cross-linked doesn't show such good characteristics. Another promising material for this application is polyimide. Recent advances in polyimide technology have delivered polyimides with curing temperatures below 200ºC. Currently, thick films (>300nm thick) are required to minimize leakage; however, given this constraint, transistors with good performance and good flexion characteristics have been demonstrated (14).

Most printable dielectrics being considered to date are relatively thick (100-300nm). This is a significant concern for organic devices. Organic semiconductors, unlike their inorganic counterparts, show significant increase in mobility with increasing transverse electric field. Therefore, to achieve the high mobilities discussed above, devices are operated at V_{DD} = 20-50V. This is problematic in both displays and RFID applications, since it greatly increases power consumption. To reduce the operating voltage, it is necessary to either reduce the dielectric thickness increase the dielectric constant. Recent results with self-assembled dielectric monolayers have produced devices with sub-5V operating voltages and good electrical characteristics (15). Along the lines of the monolayer transistor work above, there is hope that a printed self-assembled monolayer may enable the realization of low-voltage, high-performance printed devices.

An alternate approach involves the use of high-K dielectrics. Such materials enable the use of thicker (and therefore more easily printable) dielectrics while still realizing low-voltage operation. Various solution-phase routes to high-K dielectrics are currently being studied. Using an organometallic titania precursor that was subsequently thermally converted at 200ºC to realize a 100nm thick titania film (k ~ 40), we have realized transistors with operating voltages of 5V. The films are generally porous and therefore suffer from low-field leakage; however, several optimization strategies are currently being pursued, and this approach is a promising pathway to realization of low-voltage printed devices. Note that such high-K layers have an advantage over SAMs, since the converted material is insoluble and therefore free from solvent interactions.

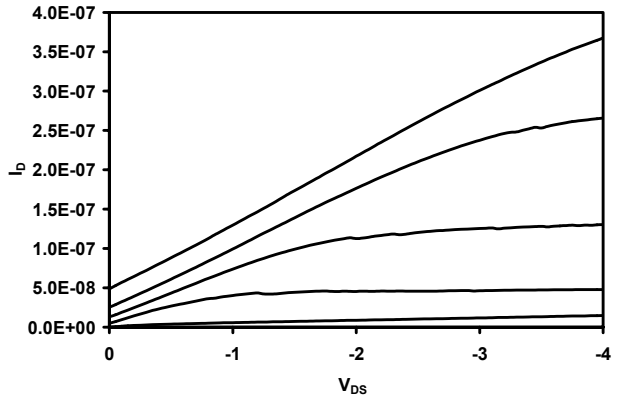

Figure 5: A low-voltage OFET using a solution-processed titania dielectric.

SUMMARY

Printed electronics is promising for realizing ow-cost flexible displays and RFID tags. Soluble oligomer semiconductor precursors provide a pathway to well-ordered crystalline films offering high-performance through a printed process. To reduce the voltages required for these devices, use of self-assembled monolayers and printable high-K dielectrics is currently being investigated, with initial results showing great promise.

ACKNOWLEDGEMENTS

This work were funded by NSF, DARPA, SRC, MARCO, Kodak, UC-SMART, and UC-MICRO. Fabrication was performed in the Berkeley Microfabrication Laboratory.

REFERENCES

1. Klauk, H. *et al*., 57th Annual Dev. Res. Conf. Dig., 162 (1999).
2. V. Subramanian, 2nd Adv. Tech. Workshop on Printing an Intelligent Future (2003).
3. P. F. Baude *et al*, IEDM '03 Technical Digest., 8.1.1 (2003).
4. S. Molesa *et al*, 2004 Mat. Res. Soc. Spring Meeting (2004)
5. B. Mattis *et al*, Proc. Mat. Res. Soc., **771**, L10.35 (2003).
6. D. J. Brennan *et al,* Proceedings of SPIE, **5217**, 1 (2003).
7. Afzali et al, JACS Comm., (2002)
8. A. R. Murphy *et al*, J. Am. Chem. Soc., (2003)
9. P. C. Chang *et al,* 62nd Dev. Res. Conf., Dig., (2004)
10. H. Klauk *et al,* Applied Physics Letters, **82**, 4175 (2003).
11. J. B. Lee *et al*, IEDM '03 Technical Digest, 8.3.1 (2003).
12. D. Redinger *et al*, 61st Dev. Res. Conf. Dig., 187 (2003).
13. S. Molesa *et al*, Proc. Mat. Res. Soc., **769**, H8.3 (2003).
14. T. Someya, IEDM '03 Technical Digest. 8.4.1 (2003).
15. H. Klauk *et al,* IEDM '03 Technical Digest. 8.2.1 (2003).