Large area, high resolution, dry printing of conducting polymers for organic electronics

Graciela B. Blanchet\textsuperscript{a)}
DuPont, Central Research, Wilmington, Delaware, 19880

Yueh-Lin Loo\textsuperscript{b)} and J. A. Rogers
Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

F. Gao and C. R. Fincher
DuPont, Central Research, Wilmington, Delaware 19880

(Received 15 August 2002; accepted 5 November 2002)

We show here that thermal imaging, a nonlithographic technique which enables printing multiple, successive layers via a dry additive process can be used in combination with tailored printable conductors in the fabrication of organic electronic devices. This method is capable of patterning a range of organic materials at high speed over large areas with micron size resolution and excellent electrical performance avoiding the solvent compatibility issues currently faced by alternative techniques. Such a dry, potentially reel-to-reel printing method may provide a practical route to realizing the expected benefits of plastics for electronics. We illustrate the viability of thermal imaging and imageable organics conductors by printing a functioning, large area ($4000 \text{ cm}^2$) active matrix backplane display circuit containing several thousand transistors. © 2003 American Institute of Physics. [DOI: 10.1063/1.1533110]

Organic electronic systems offer the advantage of low weight, mechanical flexibility, and large area coverage at potentially lower cost. Although the fabrication of functioning plastic transistors using approaches such as ink jet, dye, transfer, lithography, and stamping has been described in the literature,\textsuperscript{1–6} designing a set of chemically compatible materials that may ultimately allow for the sequential application of liquid layers, represents a major technical barrier. These material issues jeopardize the vision of printing inexpensive, throwaway plastic electronic components in a printing press and at high speeds. While the present set of materials are not suitable for printing thin film transistors (TFT) from sequential liquid layers neither can printing presses hold the resolution and registration required for device fabrication. In time, these difficulties may be surpassed and the vision of printing of organic electronics devices in a press may come to pass but that promise is, at minimum, a few years away.

It is perhaps more practical today to consider fabricating organic electronic devices with printing techniques that circumvent the serious materials and process issues presently associated with printing in a press. Thermal imaging,\textsuperscript{7} a technique that enables the printing of multiple, successive layers, via a dry additive process provides an attractive alternative path. With printing proceeding via the ablative transfer of solid layers the solvent compatibility issues that are encountered when printing sequential layers from solution are entirely avoided. Over the last ten years DuPont has developed a platform of digital products based on thermal imaging, recently commercialized digital color proofing, developed digital color filters, and currently evaluating organic electronics.

In all cases the design of the printable material set has been the key enabler.

Thermal imaging allows for the patterning of a range of organic materials at high speed, over large areas, and with micron size resolution. The imaging process, illustrated in

\textsuperscript{a)Author to whom correspondence should be addressed; electronic mail: graciela.b.blanchet@usa.dupont.com}

\textsuperscript{b)Present address: University of Texas at Austin, Department of Chemical Engineering, Austin, TX 78712.}
Fig. 1, involves the pixelized transfer of a thin solid layer, encompassing a digital image, from a donor film onto a flexible receiver. A detailed view of the film structure is also shown in the figure. The film is imaged as follows. A 40 W 780 nm infrared diode laser, split into 250 2.7 μm×5 μm individually addressable spots, is focused through the donor base at a thin metal layer. The efficient conversion of light to heat at this interface decomposes surrounding organics into gaseous products. Their expansion thus propels the top layer of the donor film onto the receiver. In Fig. 1, a gate pattern is printed by selectively transferring the individual 5 donor film onto the receiver. In Fig. 2(a), shows a transferred PANI/SWNT 20 μm line. Numerous SWNTs anchored onto the edge of the conducting line and extending into the channel are also visible. The micrograph on the upper right [2(b)] shows a single SWNT rope extending from the PANI/SWNT source line into the channel. The plot in the lower frame [2(c)] shows the conductivity, α, of the printed line, in S/cm, as a function of transfer laser fluence, in W, is shown later.

The first step towards applying thermal printing to the fabrication of an all-printed electronic device is the design an imageable organic conductor. Early experiments show that conducting polymers typically used in organic electronics, [i.e., poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid PEDOT/PSS, dodecyl benzene sulfonic acid doped polyaniline (DBSA–PANI) and camphor sulfonic acid doped polyaniline] cannot withstand the heat generated during thermal imaging. In contrast, DNNSA–PANI, a polyaniline synthesized via emulsion polymerization and doped with dinonyl naphthalene sulfonic acid (DNNSA) can be thermally imaged without backbone deprotonation. The inherently low conductivity, 10⁻⁴ S/cm, of DNNSA–PANI was increased four orders of magnitude by dispersing low concentrations of SWNT into the polymer solution. In the examples that follow we used as printable conductor 3% SWNT dispersed in DNNSA–PANI.

Figure 2(a) illustrates a 20 μm DNNSA–PANI/SWNT source line printed via thermal imaging. Individual pixels seen as discrete steps along the line edge. The micrograph also shows SWNT ropes anchored at the line edge and extending into the channel. The result suggests that pixels may carry ropes that extend beyond their volume. Then, portions of a rope lying outside the pixel being transferred become visibly exposed if the neighboring pixel is not transferred. Figure 2(b) shows a single SWNT rope well anchored onto the edge of a PANI/SWNT source line. Figure 2(c) shows that the conductivity of printed line is highly dependent on process parameters, specifically laser power. The conductivity increases from threshold at 2.5–3.5 W decreasing thereafter. The decrease in conductivity at higher fluences merely reflecting the deprotonation of the PANI backbone at elevated temperatures. Conductivity was measured using a standard four-probe method and line thickness using a profilometer.

The I–V characteristics of a printed transistor are shown in Fig. 3(a). The structure of the transistor was as follows. A 100 nm indium tin oxide (ITO) film sputtered onto a 7 μm Mylar substrate was used as the gate. A glass resin, spun onto the ITO to about 1.5 μm in thickness, insulated the gate from the printed DNNSA–PANI/SWNT source and drain. Unpurified pentacene was deposited on top via thermal evaporation. The channel width (W) and length (L) of the printed was 750 μm in and 22 μm, respectively. The gate voltage, $V_g$, was varied from 0 to −100 V in −20 V steps. Printed transistors yielded stable bottom contact devices with on/off ratios (>1000) compatible with spin-cast dielectrics.
The effective mobility of the printed device was computed from the saturation current at high voltage was 0.3 cm²/V s while the mobility of a control device with Au source and drain and similar W/L was 0.15 cm²/V s. Since SWNTs extending into the channel provide a larger surface area for the PANI to anchor the evaporated pentacene, better adhesion may also aid in a more efficient charge injection at the interface. Alternatively, the observed differences in mobility, i.e., contact resistance, may reflect differences in the charge injection mechanism at organic/organic and metal/organic interfaces.9–12 Figure 3(c) shows the I–V characteristic of one of the transistors in the large printed panel. The gate voltage, \( V_g \), varied from 0 to −100 V in 20 V steps, is specified on the right.

To conclude, the results presented here represent the demonstration that a conducting layers of a functioning organic electronic device can be printed, over large areas via the ablative, sequential transfer of solid films of conducting polymeric material. We illustrated the viability of thermal imaging and of the imageable conductors by printing a 50 cm×80 cm TFT backplane that is thin, of ultralow weight at a throughput of 1000 cm²/min. In addition to the printing of the conductor we are currently developing materials and techniques for the printing of the gate dielectric and the semiconductor itself. Although the early results are quite promising, there remains a large amount of work before either the materials or the process are refined to adequate performance standards. Nevertheless, since thermal printing eliminates masking or photolithography also avoiding the need for interlayer solvents compatibility, the results presented here suggest that thermal imaging may bring organics electronics a step closer to reality.

The authors thank J. Catron for his able technical assistance.