

Jet Printing for Large Area Electronics

*Steven Ready, William Wong, Kateri Paul, and Bob Street
Palo Alto Research Center, Inc.
Palo Alto, California*

Abstract

The advent of new solution based organic and inorganic/organic hybrid semiconductor material along with a desire for less expensive ways to produce large area electronic devices has stimulated research into non-conventional circuit patterning methods. We report on an inkjet based printing system which was constructed to facilitate the production of etch masks and electronic devices for large area applications such as displays and x-ray sensors. A multi-ejector wax print head was integrated for high accuracy, high throughput printing of etch masks and material exclusion zones in the processing of amorphous silicon and organic electronics circuitry. The same system also utilizes specialized single ejector print heads to deposit a wide variety of organic electronic materials for rapid turn experimentation required for materials and process development. Feature sizes down to 20 μm and control of feature placement below 5 μm are achieved. System design and capability will be discussed in the context of the resolution, throughput, material requirements and electronic device performance.

Introduction

Recent developments in solution based organic electronic materials have encouraged efforts in exploring the use of conventional printing methods to produce very low cost electronic devices.^{1,4} Confidence in the early maturing of this technology has spawned the creation of several companies vying for an early adaptor's advantage in market share and name recognition.⁵ Among the initial applications sited are radio frequency identification (RFID) tags and displays. The potential advantage for RFID tags is to produce these small devices at such a low cost that they will replace bar code scanning and enable many more uses.

While largely driven by the desire to integrate newly developed organic LED material, the application of printed organics to display manufacture can also be seen for its potential to greatly reduce the equipment cost, increase the throughput and provide the capability to use inexpensive flexible substrates. The Holy Grail for this technology is the realization of integrated electronics without the need for expensive vacuum deposition, etching, and lithography equipment. There are several methods borrowed from current document printing technology that can be applied to the patterning solution based organics.^{6,7} Two of the most

quoted methods are ink jet and stamping. While, jet printing is perhaps the most flexible in terms of the variety of materials and modifications to the design, most reports to date focus on single ejector applications. In most applications to large area electronics such as displays, the throughput bottleneck imposed with the use of a single ejector is prohibitive. The need for high throughput offered through parallel deposition methods without sacrificing alignment, accuracy and repeatability is crucial for this technology to succeed in applications from large area imagers to flexible displays to active/passive flex circuitry to distributed sensors on a flex medium.

Here we discuss a research system for jet printing material to produce electronic devices and circuits. Our intent is to explore new materials and processes as well as flesh out the issues for the development of a high throughput, highly reliable large area jet printing system.

System Description

The printing system consists of a high accuracy XY stage fitted with two temperature controlled vacuum chucks for substrate transport, a multi ejector wax piezo print head, and two varieties of single ejector print heads used for the application of organic electronic material. All of the print heads were taken from other print related projects and as such were not designed for this purpose. The system is also fitted with two miniature video microscopes position registered to the various print heads for alignment and verification purposes.

The system electronics are comprised of National Instruments digital IO and waveform generator PC cards capable of printing up to at 40 kHz, or 1 m/sec at 600dpi. The XY stage control electronics supply positioning and ejector triggering to an accuracy of 0.1 μm .

Wax Printing

The wax multi-ejector printhead consists of several hundred staggered piezo ejectors. The print head and wax reservoir are heated above the wax melting point of 80°C. While the wax reservoir and fluidic delivery system in the print head was designed to print horizontally, in this application the printhead is positioned over the XY stage and prints downward onto the substrate. A Kemamide based wax is ejected using waveform parameters beyond those normally specified for document printing. The resulting spot sizes are approximately 40 μm diameter. To completely fill

an area in raster fashion a minimum of 8 passes of the print head.

Under normal operating conditions for document printing, variations in spot placement can be as large as 50 μm . Modifying the waveform and wax temperature in order to produce $\sim 40 \mu\text{m}$ spots while ejecting downward did not remarkably worsen this variation. In fact, as seen in figure 1, most of the spots were within 10 μm of the expected placement. However, these ejection conditions caused a number of ejectors either to fail to eject or fail to continuously eject. This situation is made worse by the fact that a number of ejectors work or fail to work after thermal cycling. In order to provide a robust system which produced reliable ejection during a printing session as well as $\sim 1 \mu\text{m}$ spot placement accuracy, a machine vision spot placement/calibration procedure was implemented as well as a method for printing with a sparse set of ejectors. The calibration routine also allows us to extract and correct for variations due to head angular misalignment, thermal expansion of the head that can result in a run out error of up to 25 μm and an offset error which results from the time it takes for the drop to travel to the moving substrate. While the hardware has the potential to correct for variations of individual ejector drop velocity, we have not attempted to implement this yet.

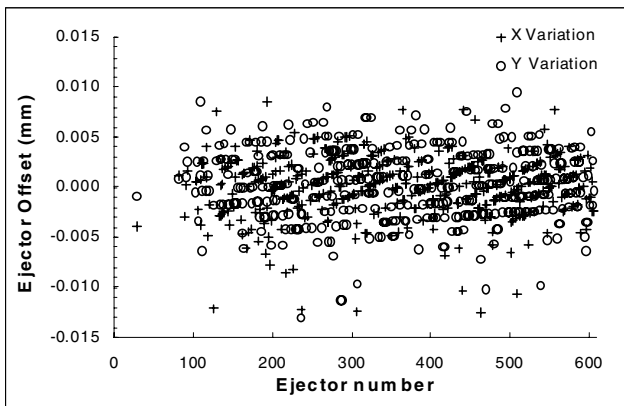


Figure 1 Variation in X and Y spot placement for the 424 working ejectors. Spots producing greater than 15 μm variations not shown

With the methods outlined above, spot placement is controlled to within $\pm 1 \mu\text{m}$. While the reduction in the number of available ejectors on the head reduces the amount of parallelism achieved, the average time it takes to print a mask layer on a 4-inch wafer is measured in fractions of minutes rather than the tens of minutes it would take for a single ejector.

Figure 2 shows a segment of an array of transistors fabricated from jetted wax mask layers of amorphous silicon/metal/dielectric material. The transistor cells are 320 μm square and perform as well as transistors fabricated from standard photolithography. For each mask layer, the single printed mask step replaced 4 standard lithography steps; spin on resist, oven bake, mask align and expose, and

strip. This method also allows for on the fly design modifications.

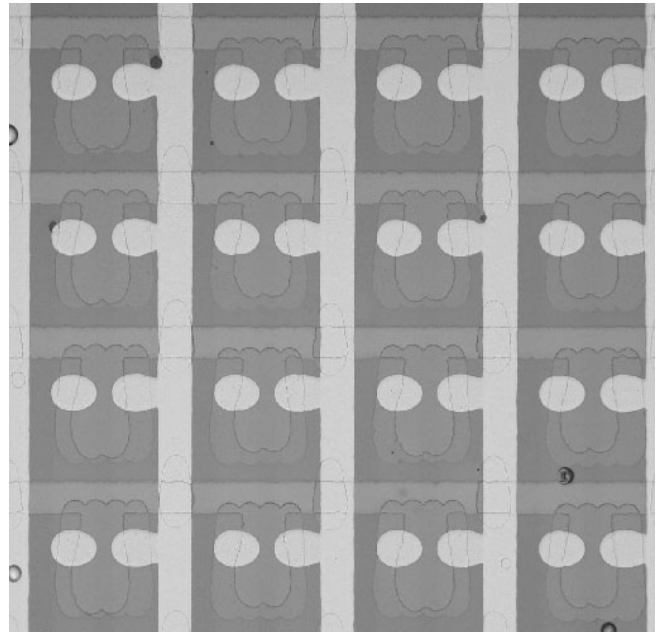


Figure 2. Jet printed wax mask defined amorphous silicon transistors on 320 μm array grid.

Single Ejector Solution Printing

Single acoustic and piezo ejectors are used to print organic electronic materials onto test circuits. In order to accommodate the variety of materials to be printed, the simple ejectors eject up onto the substrate that are fixed to a temperature controlled vacuum chuck.

The acoustic ejector⁵ (figure 3) consists of a piezo material bonded to a quartz lens submersed in the fluid to eject. The lens transmits high frequency (100-140mHz) acoustic energy and focuses the energy at the fluid surface resulting in the ejection of a drop. Similar devices have controllably produced variable drop volumes from 1 femtoliter to 10 nanoliters, with control of $\pm 2\%$.

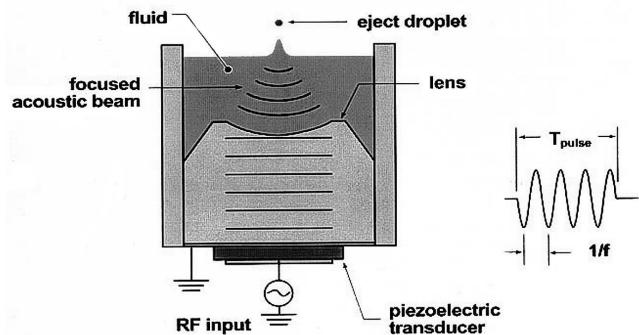


Figure 3. Acoustic single ejector schematic. The focused RF acoustic energy ejects droplets from free fluid surface

The advantage of this ejector system is the ability to eject from a relatively free fluid surface. Many of the polymers of interest are dissolved in volatile solvents (i.e. xylene, toluene), some of which require modestly elevated temperatures to maintain the polymer in solution. The availability of any free surface from which solvent can evaporate tends to build up polymer concentrations, forming a film at the fluid surface. Small nozzle apertures tend to clog while the nozzle-less surfaces survive better, particularly under relatively constant ejection.

The piezo single ejector (figure 4) in use is of all stainless steel construction with reservoir volumes as small as 20 microliters. This ejector is intended to be used initially for relatively precious material under investigation. Variations in design parameters allow for drop volumes range from 50 picoliters to 10 nanoliters, with control of $\pm 2\%$ and fluid utilization of 95%. Due to the small aperture, it is more useful for less volatile solvents and water-based solutions.

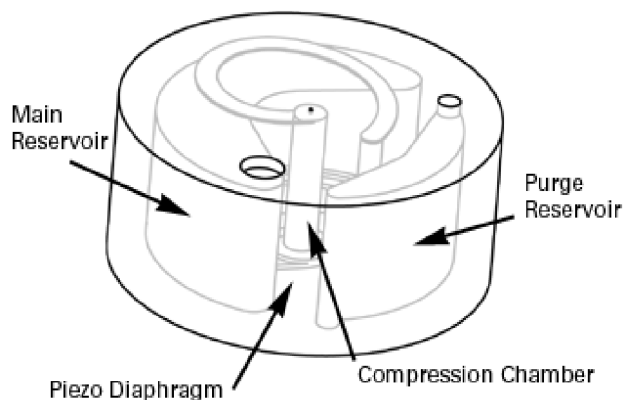


Figure 4. Single piezo ejector design. The self-contained reservoir/piezo/aperture unit is approximately 1cm in diameter.

Materials Printing

The printing of the variety of materials on the variety of surfaces poses a significant challenge to systems designers as well as researchers in the field. Feature size definition relies on control of the deposited material that can be predicted and optimized for a given ejected material on a particular surface. However, electronic devices usually require several different surface layers interacting with the material being deposited, either favorably or unfavorably.

The deposition conditions to produce well-defined features can conflict with the electronic performance of the materials. For instance, a solution of F8T2 in xylene, which needs to be heated to $\sim 40^\circ\text{C}$ in order to keep the polymer in solution, deposits into well-defined structures on a $\sim 40^\circ\text{C}$ heated substrate. However, the time it takes to evolve the xylene at this temperature does not allow the F8T2 to order, producing a poorly performing transistor with carrier mobilities 1-2 orders of magnitude lower than optimal material. Deposition of F8T2 on a room temperature substrate produces acceptable electronic behavior, but the deposition of consecutive drops produces coalescence and

area dewetting, forcing the time between consecutive drops (to allow for solvent evaporation) and thus print speeds to potentially unacceptable values. As an example of this effect, Figure 5 shows two lines of PDOT, a conductive polymer, deposited on BCB, a polymer dielectric, at different printing speeds.

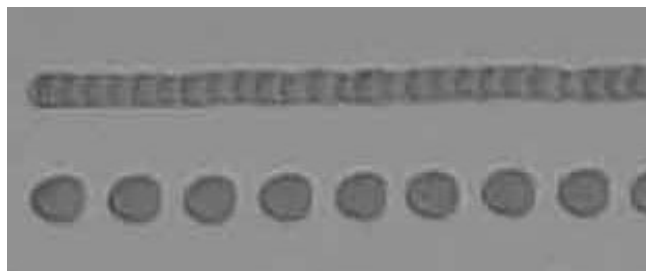


Figure 5. PDOT deposited on BCB. The bottom line was printed faster than the top line showing the effect of liquid surface tension overpowering surface wetting.

In organic as well as most other electronic materials, barriers to carrier transport such as of grain boundaries and regions of disorder are highly undesirable. Conditions that promote the formation of homogeneous material during sequential droplet deposition enhance the electrical performance. The use of coalescence, surface engineering, viscosity, solvent volatility and liquid surface tension with substrate temperature and printing speed can produce uniform lines of material with directionally enhanced performance. Figure 6 compares transfer characteristics of two transistors where the F8T2 is deposited parallel and perpendicular to the source and drain electrodes.

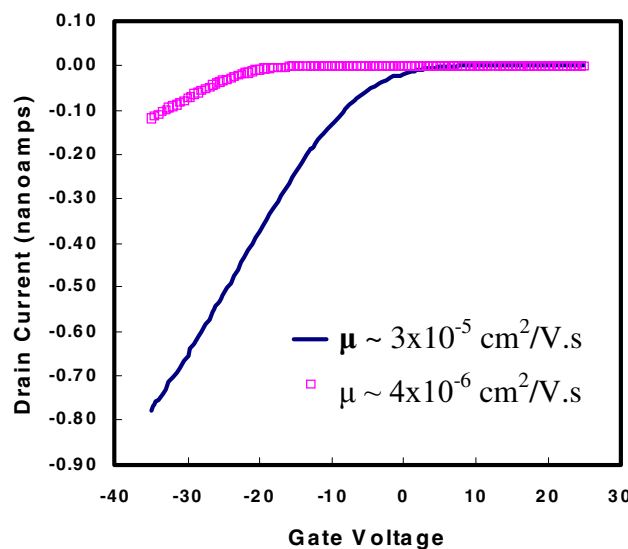


Figure 6. Transistor characteristics for jet printed F8T2 on SiO_2 . The solid line shows characteristic for F8T2 jetted perpendicular to the current direction. The boxes are from F8T2 jetted parallel to the current direction.

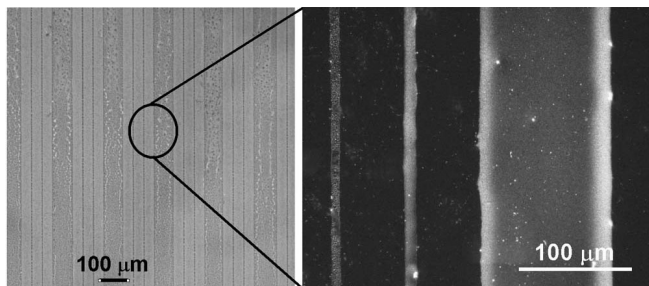


Figure 7. Wax patterned self-assembled monolayer of OTS dip coated in a fluorescent dye. The black areas are the wax patterned OTS. The thin fluorescent lines are 5-8 μm wide.

In order to circumvent and perhaps simplify the problems associated with jet printing solution-based organics, methods based on engineering of surface energies have been developed.⁸ Patterned self-assembled monolayers (SAM) have been used to organize surfaces into hydrophilic/hydrophobic areas. The solution based organic electronic material can then be dip coated, thus only adhering to the hydrophilic areas. Figure 7 shows an example where an octadecyl trichlorosilane (OTS) was applied to an SiO₂ substrate. The substrate/SAM was patterned by jetting wax. The exposed SAM was then removed from the surface prior to the wax removal. The entire wafer was then dip coated with a fluorescent dye that dewetted from the patterned OTS surfaces. In this way, feature sizes much smaller than the wax drop size can be achieved and only depend on the control of the wax drop size and placement.

Conclusion

An ink jet printing system consisting of a multi-ejector wax printhead and single ejectors for electronic polymers was presented. Methods for achieving spot placement accuracy using the multi-ejector head was discussed and accuracies of $\pm 1 \mu\text{m}$ were achieved. Examples were given on how print direction, surface properties and other parameters affect the control of features and performance.

Acknowledgements

We would like to acknowledge the contribution of Rick Stearns, Babur Hadimioglu and Scott Elrod for their help with the acoustic jet printing as well as Bob Krivacic, Bob Kowalski, Dave White and Bob Matusiak for their contribution to the development of the print system.

References

1. Garnier, F., R. Hajlaoui, et al. (1994). "All-polymer field-effect transistor realized by printing techniques." *Science* **265**(5179): 1684-6
2. Bao, Z., Y. Feng, et al. (1997). "High-performance plastic transistors fabricated by printing techniques." *Chemical Materials* 1997(9): 1299-1301
3. A few of the companies are Add-Vision, Plastic Logic, UNIAX, Universal Display
4. Wong, W.S.; Ready, S.; Matusiak, R.; White, S.D.; Lu, J.-P.; Ho, J.; Street, R.A., *APL* **80**, 610 (2002)
5. S. Elrod, C. Brown, S. Buhler, R. Ellson, J. Fitch, B. Hadimioglu, R. Kowalski, R. Matusiak, J. Roy, D. Ruiz, B. Russo, R. Sprague, M. Weisburg, D. White, M. Young, and J. Zesch, *IS&T NIP17 Proc.* 669 (2001)
6. Hsin-Hua Chang; Chung-Chih Wu; Cheng-Chung Yang; Chieh-Wei Chen; Cheng-Chung Lee, *Proc. SPIE - Int. Soc. Opt. Eng. (USA)* **4079**, 127 (2000)
7. Speakman, S.P.; Rozenberg, G.G.; Clay, K.J.; Milne, W.I.; Ille, A.; Gardner, I.A.; Bresler, E.; Steinke, *Org. Electron*, **2** 65 (Sept 2001)
8. H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbaskaran, W. Wu, E. P. Woo, *Science* **290**, 2123 (2000).

Biography

Steve Ready obtained his degree in Physics from the University of California at Santa Cruz in 1984. He then joined Xerox Palo Alto Research Center and has since studied the role of hydrogen in amorphous, polycrystalline and crystalline silicon, contributed to the development of large area amorphous and polycrystalline silicon imaging arrays for optical and x-ray applications, and is presently working on the development of organic semiconductor materials and devices.