Thermal Ink Jet Printing of Electronic Materials and Devices

David Punsalan, John Thompson, Peter Mardilovich, Chinmay Betrabet, Randy Hoffman, Greg Herman, and Thomas Lindner, Hewlett-Packard Company, Corvallis, Oregon, USA

Abstract

Hewlett-Packard has recently demonstrated that thermal inkjet (TIJ) can be used to print a large variety of materials including organic solvent based systems, colloidal dispersions of nanoparticles, inorganic precursor solutions, polymer light emitting materials, color filters, and adhesives.[1,2] This paper will discuss the integration of TIJ printed electronic materials (conductors, semiconductors, and dielectrics) to form thin-film transistors (TFTs). We have obtained field-effect mobilities of 3 to 4 $cm^2V^{-1}s^{-1}$ for TFTs with TIJed semiconductor (channel), with on-to-off ratios of 10^6 - 10^7. TIJ-deposited gate dielectrics have shown a gate dielectric breakdown field >1 MV/cm, with maximum gate current leakage ~2-5 nA/cm^2.

Introduction

The primary goal of printed electronics is to substantially reduce the cost of manufacturing of electronic devices. It is projected that several multi-billion dollar markets will result when new materials as well as processing, deposition, and patterning methods have been developed to realize this goal. These markets include displays, smart-labels, sensors, signage, and radio frequency identification (RFID) tags. Since several of these markets are extremely price sensitive, significant cost reductions are necessary before they will expand at the rates predicted.

Thermal inkjet (TIJ) printing has excellent overlap with the patterning and deposition needs of printed electronics. In combination with other low-cost process steps, this method reduces the dependence on expensive multistep photolithography processes that include deposition, pattern, and etch. Although the minimum resolution available using inkjet as a direct patterning tool will not approach that of photolithography, features approaching the micron-scale have been demonstrated (for example, features as small as 8 microns have been produced for gold conductors[3]).

Various materials have been studied in regards to their thermal inkjet printability as well as their final film performances for printed conductors, dielectrics and semiconductors. Our investigation has included the use of both commercially available and in-house synthesized precursor inks. While many paths have been investigated (including material selection, precursor formulation, and printing and post-printing processes), this paper focuses primarily on printable inorganic electronic materials for TFT fabrication. Inorganic semiconductors have several advantages over their organic counterparts, particularly with regard to attainable stability and mobility; the "off" current for organic semiconductor based TFTs is known to increase upon exposure to ambient O_2 and H_2O, thus significantly reducing the on/off ratio over time.[4]

Thermal Inkjet Printed Materials

Thermal Inkjet Printing of Non-aqueous Fluids

While the mechanism for drop ejection in thermal inkjet technology imposes some boiling point limitations on the choice of solvent, we have found through experimentation that a wide range of solvents can be readily dispensed with commercially available HP TIJ printheads. Moreover, the solvent of choice for many of the precursors and polymer solutions of interest are low molecular weight alcohols for which thermal inkjet printing is proving to be well suited.

Our development efforts involve the use of a commercially released 600 dpi printhead with 35 pL drops and 12 kHz firing frequency (HP No. 80 black ink cartridge) as well as an internally developed printhead capable of smaller drop volumes and increased printing speed.

Our printing tools include the capability for three two-ink printheads and a camera-vision system coupled with a temperature-controlled, driven X-Y-Z-θ stage and printhead-media spacing probe. Software allows semi-automatic pattern alignment with stage positional accuracy of $\pm$ 0.5 µm.

Thermal Inkjet Printed Conductors

We have successfully printed a commercially available Ag ink from Cabot [product # AG-IJ-G-100-S1] which gives exceptional performance and is readily TIJ printable after a minor reduction in viscosity with additional solvent. Figure 1 shows optical micrographs of printed Ag lines thus produced. Line widths and line-to-line gaps as small as 50 µm were fabricated with excellent sheet resistivities of less than 1Ω/sq in a single pass. As can be seen in Figure 1 (bottom), a highly reflective Ag film with a mirror-like finish was obtained.

Thermal Inkjet Printed Gate Dielectrics

The formation of gate dielectrics that have acceptable electrical properties and low defect density can be a challenge for any deposition method. We have found that dual layer, composite dielectrics fabricated via TIJ perform quite well in the TFT structure.[5] The dual layer film stack allows an optimal semiconductor-gate dielectric interface to be achieved with a first layer, while simultaneously minimizing defect density and maximizing dielectric strength by appropriate selection of a second layer (see Figure 2). Top-gate TFT structures were fabricated using traditional vacuum deposition and patterning techniques (sputtering and shadow masks) for all TFT layers with the exception of the gate dielectric, for which the TIJ deposited dual layer gate dielectric was used. These devices show qualitatively ideal IV characteristics (Fig. 2) and excellent performance, with typical peak channel mobility (μ_{inc}) ~5-15 cm^2/V s, drain current on-to-off ratio as high as ~10^6-10^7, and gate leakage below ~5 nA/cm^2.

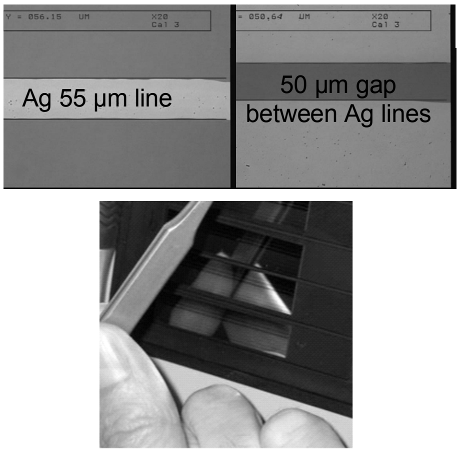

Figure 1. Printed Ag images

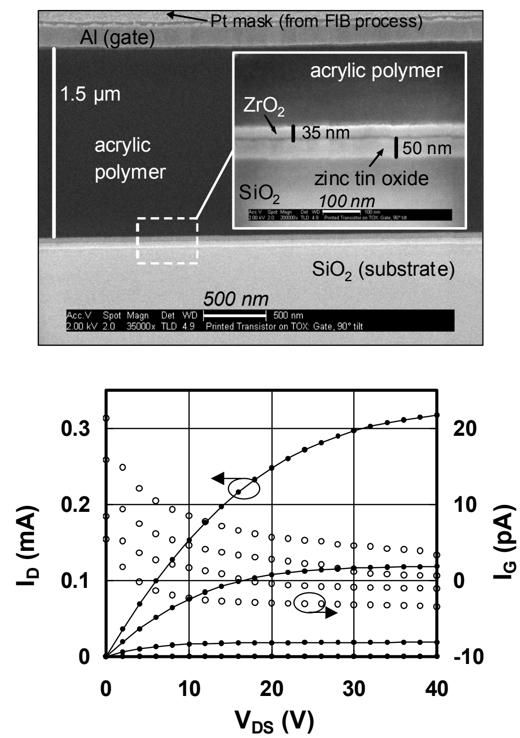

Figure 2. TIJed TFT gate dielectric. Top) focused ion beam milled cross-section scanning electron micrograph of film stack. Bottom) IV output characteristics, V_{GS} varied from -20 to 40V in 20V steps[4]

Solution Processable Inorganic Semiconductors

Precursor Development and Spin Coating vs. Thermal Inkjet Printing

At the outset of our investigation, a variety of chemistries and solvent systems were formulated to provide the necessary inks for a zinc oxide precursor. Initially the precursors were spin coated as well as TIJ printed to study any potential deleterious effects introduced by the inkjet deposition process, as has been reported for organic semiconductors. Standard bottom-gate TFT test structures with 1000Å of thermal SiO2 with sputtered source and drain electrodes were fabricated to assess the relevant electrical parameters (mobility, on-to-off ratio, turn-on voltage). The learnings from this work allowed us to focus on selected specific precursor and solvent systems. Moreover, the comparison of TIJ versus spin coated results showed no degradation in performance due to TIJ printing. After some basic optimization of the ink formulation, performance was increased two-fold, bringing the mobility to 2 cm^2/Vs, with an on-to-off ratio of 10^5 and turn-on voltage of ~ -5V.

TFT Integration Challenges

Having developed all components of the TFT (conductor, semiconductor and gate dielectric), we began integrating the materials to make a fully TIJed device. Not surprisingly, we found that every previously vacuum deposited layer replaced by TIJ printing was accompanied by a reduction in performance, specifically a reduction in drain current or increase in gate dielectric leakage current. Perhaps most importantly, substantial surface roughness on the semiconductor layer led to a poor interface with the adjacent gate dielectric layer. With the initial integration of all the layers into a fully TIJed transistor, we did observe an effect of gate voltage on drain current (i.e., a field-effect), but since the channel could not be effectively depleted of carriers, no significant on/off ratio nor saturation in I_D-V_{DS} curves was obtained.

Improved Semiconductor Morphology

Through further materials and precursor development, we were able to obtain much smoother films for the semiconductor (channel) layer, as seen in the AFM shown in Fig. 3. The observed root mean squared roughness obtained on a 4 μm^2 scan was 0.2-0.3 nm, comparable to the surface roughness attainable by vacuum deposition methods.

In addition to reduced surface roughness, significantly increased mobility was observed for the newly formulated semiconductor. Consistency in performance from device to device and die to die was also significantly improved. Devices fabricated using this ink have yielded mobilities of 4 cm^2/Vs, on-to-off ratios of 10^6 – 10^7 and turn on voltages of ~ -5V.

Using the newly formulated semiconductor precursor, as well as other advances in our conductors, gate dielectrics and process development, an all-TIJed TFT was successfully fabricated. The I_D-V_{DS} curves for the device are shown in Fig. 4. Although the drain current is relatively small, qualitatively ideal TFT characteristics are obtained, including drain current saturation and a turn-on voltage near 0 V.

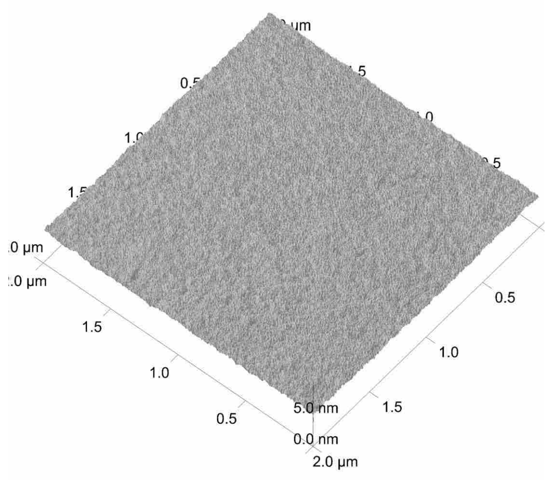

Figure 3. AFM of printed semiconductor film *(0.2-0.3 nm RMS roughness over a 4μm² scan)*

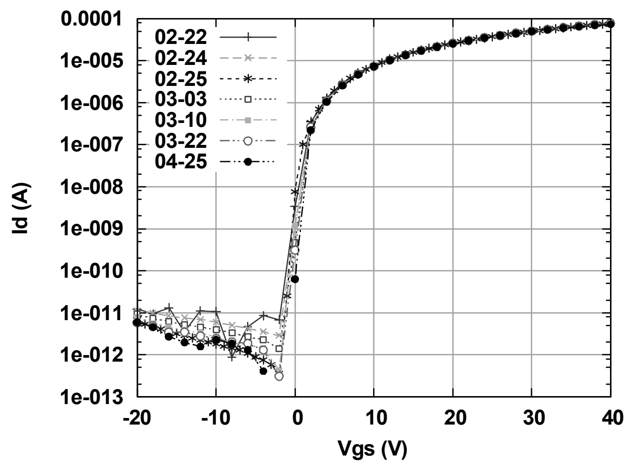

Figure 5. Stability of TIJ printed inorganic semiconductor I_D-V_{GS} transfer characteristics (V_{DS}=1 V). Dates of testing are indicated in top left corner of graph.

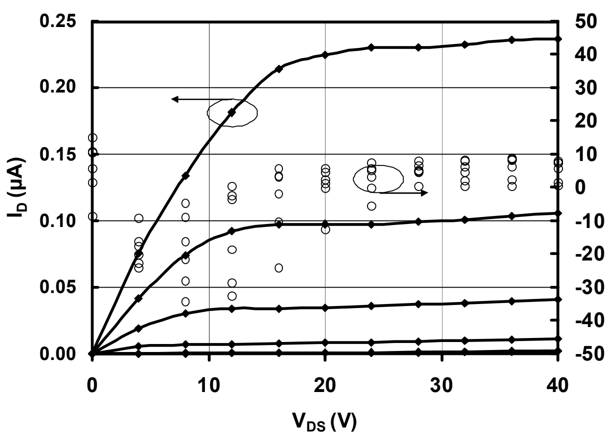

Figure 4. I_D-V_{DS} output characteristics for a fully TIJed TFT; all layers TIJ printed (gate voltage is varied from -10 to 40V, in 10V steps)

Stability

As previously stated, one of the primary advantages of inorganic semiconductor materials as compared to organic semiconductors is stability. Figure 5 shows measured I_D-V_{GS} transfer characteristics for a TFT with TIJ printed semiconductor (channel) layer test structure, which remained in storage for 2 months with no encapsulation. As is evident from the series of measurements, no substantial change in drain current, on-to-off ratios, nor resulting mobility (4 cm²/Vs) is observed.

References

1. Lindner, Thomas, "Electronic Materials printed by Thermal Ink Jet" MRS Spring Conference, Sym U, April 2004, San Francisco.
2. Lindner, Thomas "Printed Electronics - HP's Technology beyond Ink on Paper", Printed Electronics Europe 2005, Apr 2005, Cambridge, UK.
3. Wang, Yan, et al. "Maskless Lithography Using Drop-On-Demand Printing Method", SPIE Proceedings, Feb 2004
4. D M Taylor *et al J. Phys. D: Appl. Phys.*, 1991 (**24**) pp 2032-2038.
5. Mardilovich, P., Hoffman, R. "Thin-film transistors with gate dielectric deposited via thermal inkjet", Applied Physics Letters (submitted).

Acknowledgements

The authors would like to thank Curt Nelson for his work for the all TIJed device. We also would like thank our technicians Jay van Hoff for SEM analysis and David Blessing, Dan Lawson and David Volbeda for their assistance with sample fabrication and testing. Thanks also go to Jeff Nielsen, Jerry Meehan and the rest of the printer tooling group at HP Corvallis.

Author Biography

David Punsalan received his BS in chemical engineering from Tulane University in 1997 and his PhD in chemical engineering at the University of Texas at Austin in 2001. Soon after arriving at Hewlett Packard in the fall of that year, David began investigating the solution processing of inorganic electronic materials and has focused on TIJ fabrication of devices for the past two years.