Self Assembled Monolayers on Inkjet-Printed ITO

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Abstract and Introduction:

Ink-jet printing allows for cost efficient roll-to-roll manufacture of thin-film transistors (TFTs) over large areas, enabling next-generation transparent displays, touch panels, opto-electronics, and radio frequency identification [1-4].

TFT conductance and cutoff frequency scale inversely with gate length. However sub-micron gate lengths are incompatible with traditional printing techniques, which have ~ 20 μm resolution [5]. New methods have been investigated to make sub-micron gate length organic TFTs without advanced photolithography [4].

Here, we expanded that approach to treat inkjet-printed indium tin oxide (ITO) electrodes with hydrophobic octadecyltrichlorosilane (OTS) self-assembled monolayers (SAMs) to repel away a second printed ITO electrode, yielding sub-micron electrode gaps. By combining this process with a solution-processed semiconductor, a cost-effective short channel TFT can be made. In this project, we refined inkjet printing of ITO nanoparticle ink to obtain uniform printed ITO patterns, which erre annealed to minimize sheet resistance. We used OTS to selectively manipulate the wettability of printed ITO versus various substrates. The effect of SAMs was quantified by contact angle measurements.

Preliminary experiments show that it may be possible to use this process to fabricate narrow gaps between ITO electrodes.

Experimental Procedure:

A carbon-water ink was used to optimize printing parameters on a DMP-2800 Series Dimatix Inkjet printer (Fujifilm, Santa Clara, CA). An aqueous ITO nanoparticle (NP) dispersion with 18% wt ITO (In_2O_3 and SnO_2) and an average particle size of 18 nm (US Research Nanomaterials, Houston, TX) was printed on sodalime glass, SiO_2, Si_3N_4, and Parylene-C substrates. To optimize printed ITO resistance, 2 mm × 0.1 mm one-layer printed ITO patterns on glass were rapid thermal annealed (RTA) on a JetFirst 150 RTP for four minutes at temperatures of 400-600°C in O_2, N_2, or N_2:O_2 4:1. Resistance measurements were performed using applied voltages from -5V to 5V.

Selected samples were treated with a 0.2% OTS/toluene solution for 20-25 minutes followed by sequential rinsing in toluene, acetone and isopropanol. Measurements of advancing contact angle were made with a VCA Optima series contact angle instrument (AST Products, Inc., Billerica, MA).

Results and Discussion:

The printing waveform was optimized to obtain uniform ITO lines with 150 nm thickness per printed layer by tuning

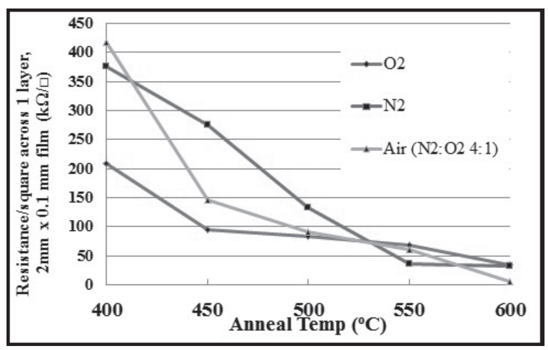

Figure 1: Printed ITO sheet resistance vs. temperature of 4-min RTA in various ambient environments.

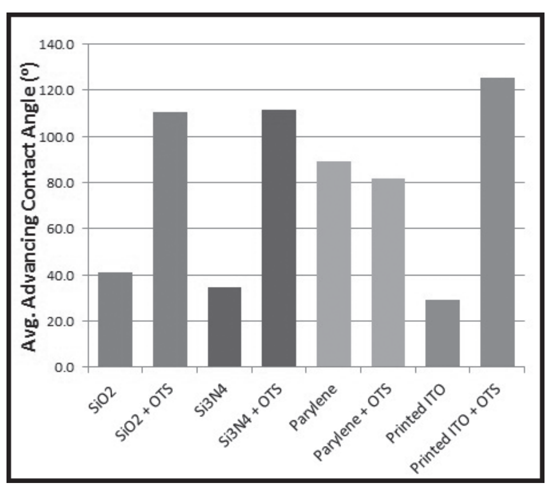

Figure 2: Contact angle of water on ITO and other substrates before and after OTS-SAM treatment.

the following parameters: firing voltages of 16-25V, firing frequency of 1-2 kHz, drop spacing of 18-20 μm and printing height of 0.5-0.75 mm. Post-printing RTA was optimized to minimize ITO resistance: four minutes at 600°C in 4:1 N_2:O_2 (air) yielded the lowest average sheet resistance of 6.1 kΩ/☐ for one-layer printed patterns (Figure 1).

Advancing contact angles of water on various substrates with and without OTS treatment were measured (Figure 2). For SiO_2 and ITO samples, contact angle increased upon OTS treatment due to OTS reaction with surface hydroxyl groups. ITO's change from relatively hydrophilic (52.77°) to notably hydrophobic (106.26°), indicates that OTS forms a SAM on ITO. The contact angle changed least for Parylene-C (88.9° before and 81.73° after OTS treatment), due its lack of a hydroxyl-terminated surface.

Selective wetting was observed between dropcast ITO and parylene after OTS treatment: the parylene could still be wetted, while the ITO film was so hydrophobic that water droplets would not leave a dispensing syringe when in contact with the ITO (Figure 3). In contrast to parylene, OTS-treatment of nitride increased its hydrophobicity, but it still remained more hydrophilic than OTS-treated ITO. Therefore, selective wetting similar to that on parylene was observed on OTS-coated ITO on nitride.

To explore the ability of OTS to define small gaps between ITO electrodes, we printed ITO patterns onto nitride substrates, annealed at 600°C for 4 min in 4:1 N_2:O_2, treated with OTS, and dropcast ITO ink. In some areas, dropcast ITO preferred nitride surfaces, however other ITO drops overlapped with OTS-treated printed ITO (Figure 4).

It is likely that the ITO drops were too large in volume to allow for very small-scale hydrophobic interactions to dominate. More investigation is needed to refine the selective wetting process.

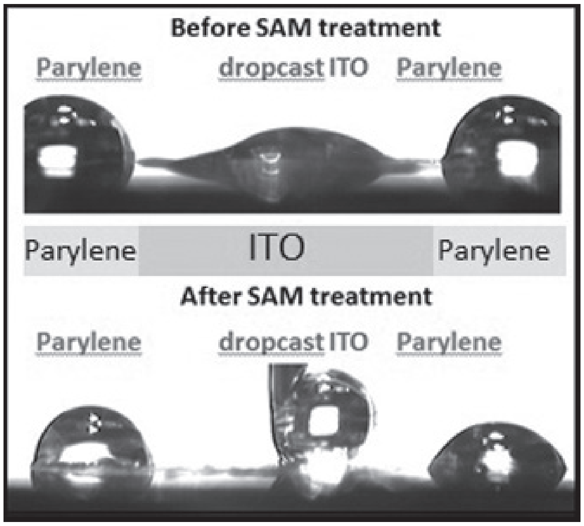

Figure 3: Water wetting on dropcast ITO and parylene before and after OTS-SAM treatment.

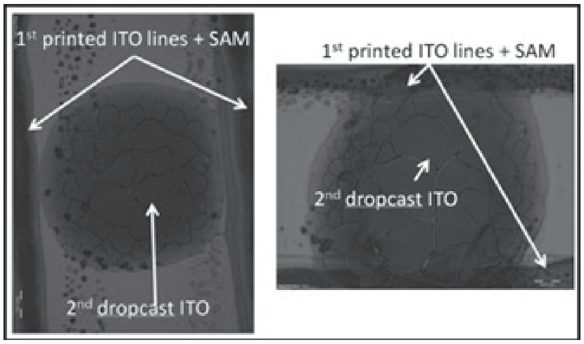

Figure 4: Different samples showing repelling (left) and overlap (right) of ITO dropcast on printed, annealed and OTS-treated ITO patterns.

Conclusions:

Inkjet printing and annealing of aqueous ITO NP inks was refined to obtain neatly patterned ITO films of thickness ~ 150 nm/layer, with minimum sheet resistance of 6.1 kΩ/☐. Contact angle measurements before and after OTS-SAM treatment show greater increase in hydrophobicity of printed ITO lines compared to substrates such as parylene and silicon nitride. We use this effect to achieve selective de-wetting of secondary ITO ink drops off previously printed ITO lines onto parylene or nitride surfaces. Preliminary results indicate that it may be possible to use such selective wetting processes to achieve sub-micron scale ITO electrode gaps, for high-performance thin film transistors fabricated by inkjet printing.

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