Inkjet Printed Silver Electrodes for Organic Thin-Film Transistors

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Abstract

Inkjet printing high resolution electrodes is crucial for printing low-cost and high performance organic thin film transistors (OTFTs). This paper reviews our recent studies on inkjet printing high resolution silver electrodes (both narrow electrodes and small gaps between the electrodes as OTFT channel length) from either a silver complex composition or a silver nanoparticles ink for OTFTs. High performance devices with a narrow electrode (< 50 um) and a small channel length (~ 10 um) were demonstrated. OTFTs with these printed silver electrodes exhibited high performance.

Introduction

Organic thin-film transistors (OTFTs) have attracted extensive interest in recent years for their potential as low-cost alternatives to -silicon transistors for large-area and flexible electronics, for instance, electronic papers and RFID tags. The economic advantage of OTFTs stems from low-cost fabrication, using common solution-based deposition techniques such as spin coating and ink jet printing. Although significant progresses have been made in past decade,[1-3] challenge and issues remain in materials, printing processes, and device integration.

As to printable conductors, earlier work was focused on organic materials such as polyaniline[4] and PEDOT doped with PSS.[5] Besides their potential thermal and electrical instabilities, these materials generally have very low conductivity less than10 $S.cm^{-1}$. In view of solution-processability, conductivity, and electrical stability, metal such as gold [6,7] or silver electrodes derived from solution-deposited precursor compositions would be ideal. Several research groups including Xerox have been exploring the use of silver complex or silver nanoparticles as conductor precursor composition for OTFTs.[8-13] Inkjet printing has been shown to have great potential as a method to fabricating OTFT devices due to its ability to print multiple components on a layer-by-layer basis with the potential for very high resolution. In this paper, we review our recent studies on inkjet printing high resolution silver electrodes (both narrow electrodes and small gaps between the electrodes as OTFT channel length) from either a silver complex composition or a silver nanoparticles ink for OTFTs application.

Results

1. Printed electrodes using silver complex

We have shown previously that highly conductive silver film can be obtained from a silver complex composition comprising silver acetate, ethanolamine, and long chain (>9 carbon atoms) carboxylic acid in n-butanol and ethylene glycol co-solvents. This silver film was first patterned into electrodes using mechanical approach, which functioned well as electrodes for OTFTs.[10] We recently investigated the inkjet printing of this silver complex as electrodes for OTFTs. Various effects such as the substrate surface properties, the concentration of each ingredient, and the printing conditions were studied in detail. [11]

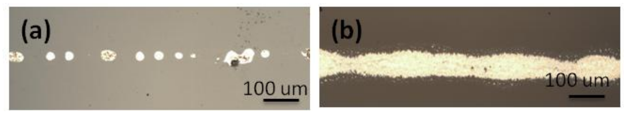

Figure 1. *Optical images of printed silver complex on (a) octyltrichlorosilane modified glass and (b) HMDS-modified glass.*

For this silver complex composition with alcohol-based solvents, it was found that the surface energy of substrate had a dramatic influence on printing results. Inkjet printing directly onto a glass slide with an advancing water contact angle of < 30° resulted in a very broad line, while printing on octyltrichlorosilane (OTS-8) modified glass having a water contact angle of ~90° showed a dotted line (Fig. 1a). Ideal printing surface would be hexamethyldisilazane (HMDS) modified surface with a water contact angle of 60-70° (Fig. 1b). These results indicated that the choice of a proper surface is important for this alcohol-based silver complex composition.

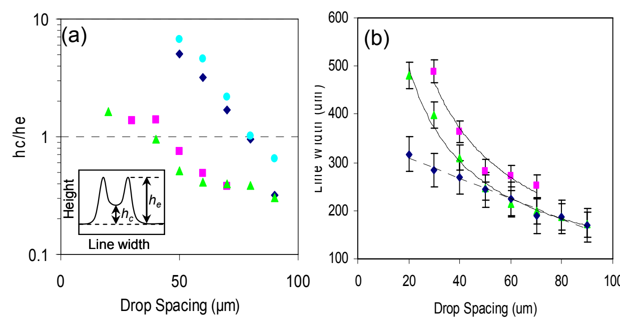

Figure 2. *(a) Effect of dot spacing on morphology of line for various ethylene glycol concentrations (▲ = 6.57%, ■ = 13.16%, ♦ = 19.74%, ● = 26.32%). Inset illustrates a typical line under the influence of the coffee ring effect. (b) Effect of dot spacing on line width for various ethylene glycol concentrations (▲ = 6.57%, ■ = 13.16%, ♦ = 19.74).The silver complex composition contains 12.5 wt% silver acetate.*

Effects of various components of the silver complex composition and printing conditions on printed silver lines were investigated in detail.[11] For example, Fig. 2a shows the effects of dot-to-dot spacing and ethylene glycol concentration on the centre/edge height ratio (hc/he) of the printed line with a 10pL nozzle. This ratio was used to quantify the movement of solute during drying and annealing, and was calculated as the average height of the center divided by the average height of the two edges.

It is evident for all dot spacings that increasing the ethylene glycol concentration resulted in less solute moving to the edges (increasing hc/he). At the optimal hc/he (~1.0), a large dot-to-dot spacing could be used when a high concentration of ethylene glycol was used. Meanwhile, the dot-to-dot spacing had a strong influence on the line width as shown in Fig. 2b. The line width decreased with increasing the dot spacing. Since it is desired that the printed silver lines be as thin as possible, high ethylene glycol concentrations such as 19.74% or 26.32% are recommended, as these conditions yield an hc/he value of 1 at the highest drop spacing, and thus the narrowest line width. With this high ethylene glycol content, we achieved the optimal film uniformity at a dot-to-dot spacing of 80 •m with resulted in a line width of 190 •m.

Further decreasing electrode width was achieved by increasing viscosity of the silver complex composition, since increased viscosity reduces the amount of spreading which occurs when a droplet impacts the substrate surface. When the silver acetate concentration was increased from 12.5wt% to 26 wt%, viscosity of the silver complex composition increased from 9.5 to 25.6 cp. As a result, the printed line width decreased to just over 100 •m. Interestingly, when this composition was printed on silicon wafer, a much smoother surface, the line width decreased further to only 60 •m.

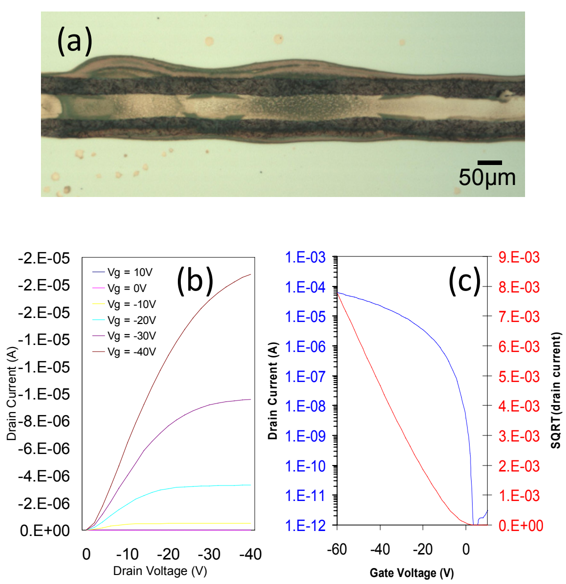

Figure 3. (a) Optical microscope image of a transistor with printed silver electrodes and PQT-12 semiconductor. (b) Output curves and (c) transfer curve of the transistor with a channel length of 1900 µm and channel width of 40 µm.

This silver complex composition is a pure solution which enables the use of very small nozzle without nozzle clogging issue. When the optimized silver complex composition was jetted with 1pL nozzle, as shown in Fig. 3a, silver lines as narrow as 40 •m were obtained. These lines were very conductive, and showed very smooth edge and uniform morphology.

OTFT devices were built onto heavily doped n-type silicon wafer (gate) with a 200-nm SiO2 layer (dielectric). The printed silver lines were used as the source and drain electrodes, and a polythiophene, PQT-12, was used as the semiconductor. The wafers were initially modified with HMDS in order to achieve the proper surface energy for printing uniform line. Following printing and annealing of the electrodes, the surfaces were plasma cleaned and modified with octanethiol and OTS-8. This modification was found to be a necessary step, as semiconductor deposited directly onto HMDS modified surfaces gave much lower performance. We have shown previously that octanethiol modification of gold source drain electrodes helped reducing contact resistance,[7] and OTS-8 is the best choice for dielectric surface modification.[14, 15] Following modification, PQT–12 semiconductor was deposited using either spin coating or inkjet printing. The devices fabricated using the spin coated PQT–12 yielded very high performance, with a hole mobility of 0.1 cm2 V-1 s-1 and an on/off ratio of 107. This performance is similar to that obtained using spin coated silver precursor,[10] indicating that no additional contact resistance was incorporated due to inkjetting of the electrode. Fig.3b and 3c shows the output and transfer curves obtained using ink jetted PQT–12 semiconductor layer. The devices fabricated with this method also yielded high performance, with a hole mobility of about 0.05 cm2 V-1 s-1 and an on/off ratio of 106. The performance is in line with ink jetted PQT-12 transistors with gold electrodes. [16]

2. Printed electrodes using silver nanoparticles

Silver nanoparticles represent an appealing alternative to printing conductive component for OTFTs. We developed a facile synthesis of stable silver nanoparticle having particle size of < 10 nm,[12] which involved reduction of silver acetate with substituted hydrazine(e.g. PhNHNH2) in the presence of 1-alkylamine (e.g. C16H33NH2) in refluxing toluene. Silver nanoparticles prepared in this manner were stable at room temperatures and were soluble in common hydrocarbon solvents.

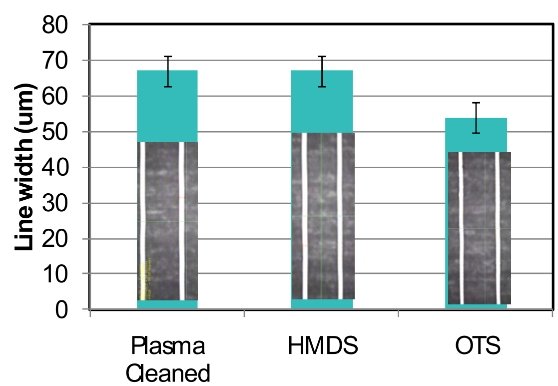

Figure 4. Line width of printed silver nanoparticles on difference surfaces. Inset, optical microscope images of the printed silver lines.

In contrast to silver complex composition, the silver nanoparticles in hydrocarbon solvents such as dodecane could be printed onto various surfaces with different surface energy. As showed in Fig 4, uniform line could be obtained on either plasma cleaned glass substrate, HMDS modified, or OTS-8 modified glass, although the advancing water contact angle of the surfaces varies from about < 30° to about 95°. There was a slight reduction of line width from about 70 µm on plasma cleaned glass to about 50 µm on OTS-8 modified glass. This surface energy independent printability is a very attractive characteristic for printable conductive materials for multilayered devices such as OTFTs, since conductive components have to be printed on difference surfaces such as substrate, dielectric, and/or semiconductor surfaces which usually have different surface energy. This unique feature was attributed to the relatively low surface tension of this silver nanoparticle ink based on hydrocarbon solvents, as the alcohol-based silver complex composition and other commercial alcohol-based silver nanoparticle ink are very sensitive to substrate surface energy. The low surface tension of the ink enables a good wetability of different surfaces. A detail study of the ink surface tension and substrate surface energy is underway.

The ability to printing on non-modified surface led to another interesting self-correction phenomenon using the alkylamine stabilized silver nanoparticle ink.[13] By taking advantage of the dynamics of a droplet impacting a solid surface during printing, the kinetic energy contained within the droplet drives it to spread to a maximum radius, after which the surface tension of the ink and the surface energy of the substrate drive the droplet to recede to a final radius which is smaller than the maximum radius. We hypothesized that it may be possible to include a surface modification agent in the ink which would modify a hydrophilic substrate during this spreading, resulting in a hydrophobic boundary surrounding any printed feature. This hydrophobic boundary would then repel any ink subsequently deposited in the proximity of the original printed feature, resulting in a self aligned channel. Fig.5a shows the self-correction printed small channel. The short line was printed first, followed by printing the long line. As one can see that the long line was automatically curved around the short line, giving a small and uniform gap between the two lines which serves as a transistor channel. To further illustrate the localized modification that creates surface energy contrast, a silver line was printed on a plasma cleaned glass slide, followed by applying a 4 μL droplet of water beside the silver line. As we can see from Fig 5b that the water could not wet around the silver line, with the water contact line repelled to about 50 μm away from the silver, clearly indicating a surface energy difference.

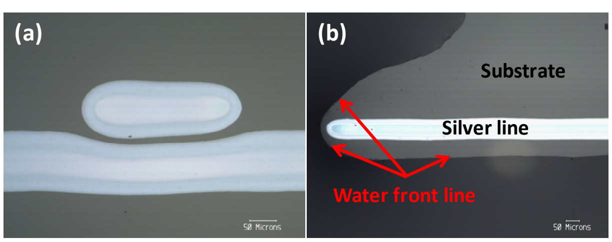

Figure 5. *(a) Optical microscope image of two printed silver lines on glass substrate, creating a narrow channel. (b) Optical microscope image of water drop around a printed silver line showing a ~50 μm hydrophobic boundary around the printed silver.*

Furthermore, this self alignment method automatically compensates for small printing errors or irregularities in the original printed electrode allowing for transistor arrays to be printed with not only very narrow channel length distribution but also high yield. This could be particularly interesting for the development of a complete roll-to-roll fabrication process. To demonstrate this, a 10x10 array of source and drain electrodes were printed using this new ink formulation with self-alignment capability. The printed source/drain arrays are shown in Fig 6a. The channel lengths of the 100 transistors in this array were measured at three locations for each transistor. These measurements were plotted as a histogram, shown in Fig. 6b. The transistor array showed a small channel length of 15 μm and a narrow channel length distribution.[13] Misfired droplets which occurred during printing had little influence since the subsequent printed features self-aligned at a constant distance away from them, allowing for a consistent channel length in spite of printing errors. We were able to achieve 100% device yield without any shorting between the printed source and drain electrodes. By properly modifying the dielectric surface and silver electrode, this transistor array with PQT-12 semiconductor showed an average mobility of $0.07 cm^2/Vs$ with some devices up to $0.1 cm^2/Vs$ and on/off ratios of 10^6, which are in line with the best inkjet-printed PQT-12 transistors.[16] Although other printing techniques were explored for high resolution electrodes before,[17-19] we first time demonstrated a facile self alignment printing technique without complicated intermediate processing steps for fabricating very reproducible small channel lengths for OTFTs.

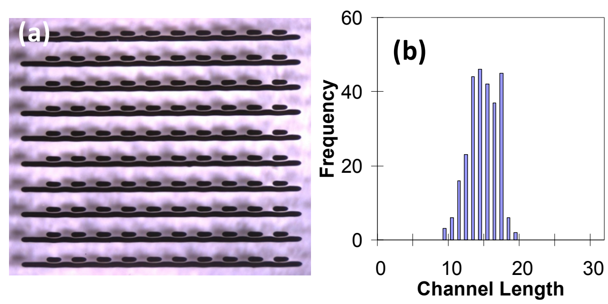

Figure 6. *(a) Optical microscope image of a 10X10 transistor array printed using the silver nanoparticle ink. (b) Histogram showing distribution of channel lengths for the transistors in the array.*

Summary

In conclusion, we have shown that high resolution electrodes can be printed from both silver complex composition and silver nanoparticle inks. The complex is a very simple approach without any synthesis steps, and it enables the use of very small nozzles. Although the printing is surface-energy dependent, by choosing a proper surface, uniform and high resolution electrode down to 40 μm could be achieved. On the other hand, alkylamine stabilized silver nanoparticle inks showed surface-energy independent printability, which enables the use of the same ink to print different conductive components on difference surfaces. When printed on a non-modified substrate, the alkylamine stabilized silver nanoparticle ink exhibited a self-alignment nature due to local modification of the substrate, which allows for large-area, defect-free source drain arrays to be printed with a narrow and uniform channel length. OTFTs with electrodes printed from both silver complex and silver nanoparticles showed high performance.

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Yiliang Wu received his Ph.D. degree from the Tokyo Institute of Technology, Japan, in 1999. After two years postdoctoral studies at Queen's University, Canada, he joined Xerox Research Centre of Canada as a research scientist to kick start materials and processes for organic thin film transistors. Currently, Dr. Wu is a Principal Scientist at the centre, leading Xerox's Printable Electronic Materials project. He is the holder of 92 US patents, and author/co-author of 80 peer-reviewed papers, 1book, and 2 book chapters.