Development of Silver Nanoparticle Ink for Printed Electronics

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Abstract

Printable conductors with high conductivity would be critical for low-cost printed electronics. In view of printability, conductivity, and electrical stability, metal such as gold or silver derived from solution-deposited precursor compositions would be an ideal candidate. Xerox has been exploring the use of silver nanoparticles as conductor precursor composition for printed electronics. This paper reviews our research in the development of alkylamine-stabilized silver nanoparticles that can be sintered at low temperature (~ 120 °C) for high conductivity (>10000 S/cm). Silver nanoparticle ink formulations based on these silver nanoparticles exhibit surface-energy independent printability which enables the fabrication of high-performance top-contact transistor devices, and self-assembly characteristic when printed on hydrophilic substrates which allows for large-area, defect-free source drain arrays to be printed with a narrow and uniform channel length.

Keywords: Silver Nanoparticles, inkjet printing, conductivity, printed electronics, thin-film transistors.

Introduction

In recent years, there has been a tremendous interest in developing solution-processable electrically conductive materials for low-cost, large-area and flexible electronic devices (e.g., flat-panel displays, wearable electronics, RFID tags) as printed conductive elements (electrodes, pixel pads, conductive tracks and lines, etc.).[1-10] Earlier work on printable conductors was focused on organic materials such as polyaniline[1] and PEDOT doped with PSS[2]. Besides their potential thermal and electrical instabilities, these materials generally have very low conductivity less than 10 S/cm. In view of solution-processability, conductivity, and electrical stability, metal such as gold[3,4] or silver[5-10] electrodes derived from solution-processable precursor compositions would be ideal.

Metal nanoparticles such as gold nanoparticles have been used as a printable precursor for fabricating high-conductivity thin-film conductors at relatively low sintering temperatures.[3,4] This approach works well because (i) the melting temperature of metals such as gold decreases drastically when the particle size is in the nanometer regime (<10 nm);[11] and (ii) gold nanoparticles can be properly stabilized with readily detachable stabilizers such as alkanethiols.[3] However, gold nanoparticles would be too costly when used for conductive tracks and lines as interconnects or pixel pads. Accordingly, significant efforts are currently being directed to printable silver materials as an alternative, since silver has the conductivity, oxidative stability, and mechanical durability characteristics, etc. to satisfy both the functional and cost requirements for printed electronics.

In this regard, electroless deposition of silver coupled with microcontact printing has been explored,[5] but this approach is too complex to be useful. Liquid processable silver pastes and inks have also been actively investigated, but they have provided relatively low conductivity (≤ 2000 S/cm) even at high annealing or sintering temperatures (>200 °C).[6] This is largely due to the voids and/or residual stabilizers present in the conductors, which disrupt the continuity of the conducting network. The voids are a result of large particle sizes which do not provide sufficient particle-to-particle coalescence. Insufficient coalesced large particles also lead to conductor surface roughness which is undesirable for multilayered device fabrication. Accordingly, low-cost printable materials that enable smooth and highly conductive thin-film conductor design are particularly sought after for printed electronic applications. For flexible electronic devices, a sintering temperature significantly below 200 °C, ideally below 140 °C, is also considered a necessity since plastic substrates suitable for flexible device design would suffer irreversible dimensional damages beyond this temperature. To fulfill these requirements, Xerox has been exploring the use of silver complex[7,8] or silver nanoparticles[9,10] as conductor precursor composition for printed electronics in past years.

Inkjet printing has been shown to have great potential as a method to fabricating electronic devices such as organic thin film transistors (OTFTs) 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 work in the development of silver nanoparticle inks for printed electronic applications. OTFT device was used as an example for demonstration of inkjet printing the silver nanoparticle ink as a conductive element. High resolution silver electrodes with both narrow electrode width and small gaps between the electrodes as OTFT channel length were achieved.

Results and Discussion

We developed a facile synthesis of stable silver nanoparticle having particle size of < 10 nm, which involved reduction of silver acetate with substituted hydrazine(e.g. $PhNHNH_2$) in the presence of 1-alkylamine at a mild reaction temperature (e.g. 60 °C).[9] The reduction was generally completed in about 1 h to give a dark brown solution which yielded a black solid of alkylamine-stabilized silver nanoparticles after simple purification. Silver nanoparticles prepared in this manner were stable at room temperature and were readily dispersible or soluble in common organic solvents such as hexane, cyclohexane, toluene, and THF. Compared to other preparative procedures for silver nanoparticles,[12-15] the present synthesis offers several advantages: (i) easy purification; (ii) low reaction temperature and short reaction time; (iii) no additional surfactants required, which eliminates contamination of final product; (iv) lower cost owing to use of less stabilizer and solvent and relatively inexpensive starting materials.

The silver nanoparticles obtained from the reaction were characterized with UV-vis spectroscopy and transmission electron microscopy (TEM). UV-vis spectra of the silver nanoparticles in cyclohexane displayed absorptions with $\lambda_{max} \sim 417 – 437$ nm, characteristic of surface plasmon absorption from metallic silver clusters.[16] TEM images showed particle size of < 10 nm in diameter for these silver nanoparticles (**Figure 1a**). Uniform thin films of ~ 50 – 200 nm could be prepared from a dispersion of silver nanoparticles in toluene (10 - 15 wt %) by spin coating on a substrate such as silicon wafer or glass slide. The resulting reddish brown film of silver nanoparticles could be transformed into a shinny silver mirror upon heating on a hotplate for a few minutes at ~120 °C. The resulting thin film was comprised of a continuous phase of coalesced or fused silver particles as clearly seen in the SEM image (**Figure 1b**). X-ray diffraction (XRD) patterns of the annealed thin film displayed diffraction peaks at 2θ = 38.1, 44.2, 64.34, and 77.39 degrees which are identical to those of a vapor-deposited silver thin film (**Figure 2**). The silver nanoparticles of this type provided annealed thin films with electrical conductivity over 2.5×10^4 S/cm as measured by conventional four-probe technique. This level of conductivity, which is in the same order as that of a vapor-deposited silver thin film of similar thickness (4×10^4 S/cm), should be sufficient as conductive elements for most electronic applications.

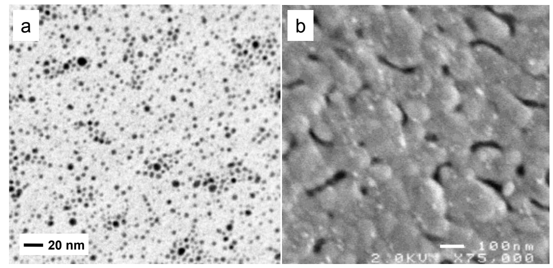

Figure 1. (a) TEM image of silver nanoparticles on copper grid; (b) SEM image of a thin film of silver nanoparticles after annealing at 120 °C for 10 min.

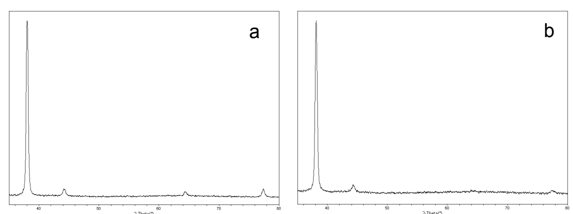

Figure 2. XRD patterns of silver thin films from: (a) silver nanoparticles annealed at 160 °C for 1 min; (b) vapor deposition.

Inkjet printable inks were formulated by dispersing the alkylamine–stabilized silver nanoparticles in hydrocarbon solvents with proper additives to adjust the viscosity and surface tension. Inkjet printing was carried out using DMP-2831 printer equipped with 10 pL cartridge. We first investigated the effects of various factors such as the substrate temperatures, the concentration of silver nanoparticles, and the printing conditions on printed line performance. Two important parameters were used to evaluate the printed lines: the line width and the film uniformity. One of the largest detractors from film uniformity is the propensity of solute to migrate towards the edge of a drying droplet. This migration, so-called the “coffee ring effect”, is induced by a higher evaporation rate at the edge with respect to the center of the droplet. To quantify the coffee ring effect, a parameter of Edge/Centre ratio (h_e/h_c) was defined as the ratio of the average thickness of the outer 50% of the line to the average thickness of the central 50% of the line in cross-section profile of the annealed line.[8] At optimal film uniformity, the h_e/h_c value should be 1.0. **Figure 3** shows the printed line width and uniformity as a function of substrate temperature at a constant drop spacing of 40 µm. For both inks, the line width decreased linearly with the increase of the substrate temperature, while the h_e/h_c increased with the increase of substrate temperature. For a given ink, there is an optimal temperature that the h_e/h_c value is around 1.0, namely, no coffee ring effect. Ink with the higher silver nanoparticle concentration offered a narrower printed line and wider temperature latitude for uniform line. We therefore use this ink to print OTFT devices.

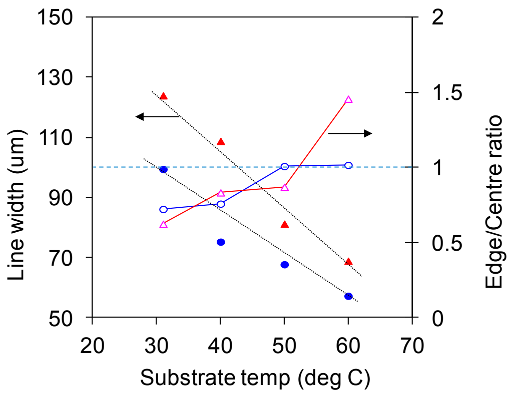

Figure 3. Printed line width (full symbols) and uniformity (open symbols) as a function of substrate temperature for two different inks. Triangle, ink with 40 wt% silver nanoparticles; circle, ink with 50 wt% silver nanoparticles.

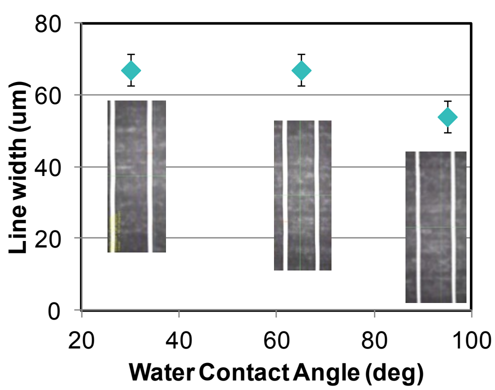

Figure 4. Line width of printed silver nanoparticles on difference surfaces. Inset, optical microscope images of the printed silver lines.

For printed electronics integration, conductive materials have to be printed on a variety of surfaces such as substrate, semiconductor, or dielectric which have different surface energies. We therefore tested the printability of our silver nanoparticle ink on different surfaces. Glass slide were used as the substrate, and the surface of glass was treated in different ways so that it had different surface energies, as indicated by the advancing water contact angle. As showed in **Figure 4**, uniform line could be obtained on either plasma cleaned glass substrate (contact angle of 30°), HMDS modified (contact angle of 65°), or OTS-8 modified glass (contact angle of 95°), 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. The results clearly indicated that our silver nanoparticle ink has surface-energy independent printability. This is in contrast to other silver inks that uniform line could be obtained only on the substrate having specific surface energy.[17]

This surface energy independent printability is particularly attractive for printing conductive materials for multilayered devices such as OTFTs, since conductive components have to be printed on different surfaces such as substrate, dielectric, and/or semiconductor surfaces which usually have different surface energy. For example, although inkjet printing techniques were explored for printing high resolution source/drain electrodes for OTFTs before, most of these studies were limited to bottom contact devices.[18,19] For top-contact OTFTs, printing continuous source/drain electrodes on top of semiconductor is very challenging. This is because (i) most organic semiconductors have a hydrophobic surface which is hard to print a continuous line on, and (ii) the solvents used in conductive inks would affect the properties of the semiconductor film, thus significantly lowering device performance. To overcome these challenges, printing silver nanoparticles with subfemtoliter inkjet nozzles was conducted to define the top metal contacts, by taking the advantage of fast drying-off the solvent in such a small volume.[20] We demonstrated here that high-performance top-contact OTFTs could be fabricated by printing our silver nanoparticle ink with normal picoliter inkjet nozzles on top of a polythiophene semiconductor, poly(3,3'''-didodecylquarter thiophene) (PQT-12)[21]. The ability to print on a hydrophobic surface and the low annealing temperature of our silver nanoparticle ink are the key enablers. **Figure 5a** shows the optical image of an OTFT with printed silver source/drain electrodes on top of spin coated PQT-12 semiconductor layer. One can see that smooth electrodes with well defined transistor channel were achieved. The channel length was about 20 µm. The transfer curve of the device (**Figure 5b**) showed close to zero turn-on voltage, high current on/off ratio, and good saturation at high gate bias. The mobility was calculated to ~0.15 cm^2/V.s in the saturated regime, which is identical to the device having vapor evaporated gold electrodes on top of spin coated PQT-12 semiconductor.[21,22]

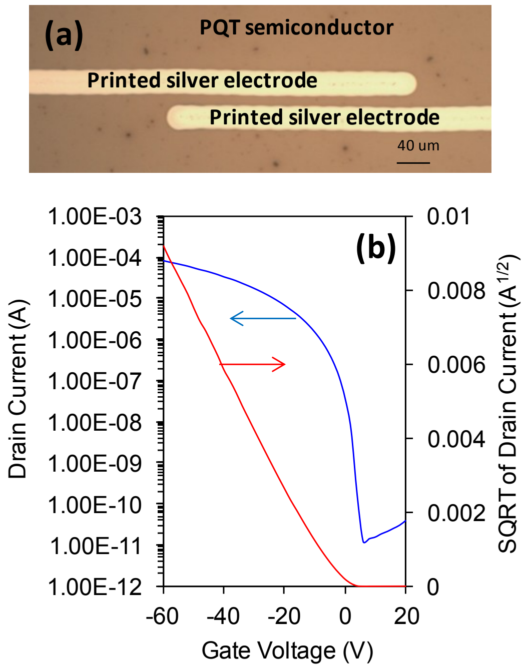

Figure 5. (a) OTFT with silver source and drain electrodes printed on top of PQT-12 semiconductor layer. (b) Transfer curve of the OTFT with the printed silver electrodes.

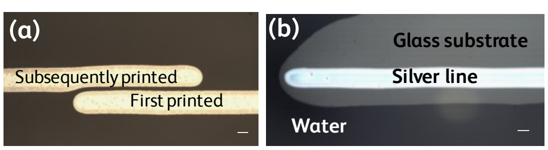

Figure 6. (a) Optical microscope image of two printed silver lines on glass substrate, creating a narrow channel. (b) Optical microscope image of water drop around a printed silver line showing a ~50 µm hydrophobic boundary around the printed silver. Scale bar: 50 µm.

The ability to printing on non-modified surface led to another interesting self-correction phenomenon using the alkylamine-stabilized silver nanoparticle ink.[23] 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. **Figure 6a** shows the self-correction printed small channel. The bottom line was printed first, followed by printing the other line. As one can see that the line printed subsequently 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 **Figure 6b** 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.

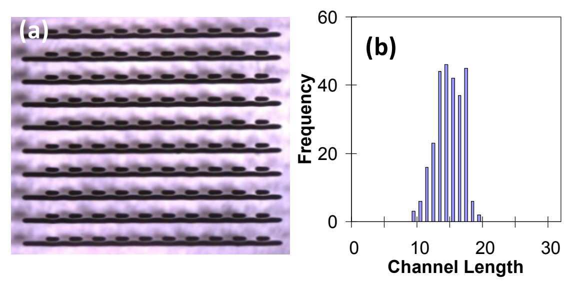

Figure 7. (a) Optical microscope image of a 10X10 transistor array printed using the silver nanoparticle ink. (b) Histogram showing distribution of channel lengths for the transistors in the array.

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 **Figure 7a**. 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 **Figure 7b**. The transistor array showed a small channel length of 15 µm and a narrow channel length distribution.[23] 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 0.07cm^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.[24] Compared with previous printing techniques for high resolution electrodes,[18-20] this is a facile self alignment printing technique without complicated intermediate processing steps for fabricating very reproducible small channel lengths for OTFTs.

Conclusion

We have shown a facile method to synthesis alkylamine-stabilized silver nanoparticles with particle size less than 10 nm. These stable nanoparticles could be sintered at a plastic-compatible temperature (e.g. 120 °C), yielding highly conductive silver features. Inks based on alkylamine-stabilized silver nanoparticles were able to print narrow and uniform lines. More importantly, the silver nanoparticle ink showed surface-energy independent printability, which enables the use of the same ink to print different conductive components on difference surfaces. The ability to print on hydrophobic surfaces enables the fabrication of top-contact OTFTs, showing identical performance to devices having evaporated gold electrodes. 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.

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