

A Simple and Efficient Approach to a Printable Silver Conductor for Printed Electronics

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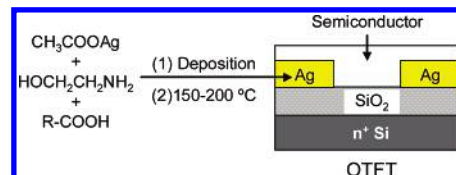
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Printed thin-film transistor (TFT) circuits have in recent years received fast growing interest as low-cost alternatives to conventional silicon-based technologies to enable ubiquitous large-area, flexible, and ultra-low-cost electronics.¹ One of the critical materials for printed TFT circuits is a solution-processable electrical conductor. However, the latter has so far received disproportionately far less attention than printable semiconductors,² despite the fact that it is equally important as conductive features (e.g., electrodes, conductive lines, and interconnects, etc.) in enabling low-cost TFT circuits.^{3–5} Scattered earlier works on solution-processable conductive materials focused largely on doped conjugated polymers such as polyanilines,^{5a} polypyrroles,^{5b} PEDOT,^{5c} etc., which are not suited for these applications due to low electrical conductivity and poor electrical/thermal stabilities. On the other hand, noble metals such as gold and silver, which possess high conductivity ($\sim 10^4$ – 10^5 S cm^{-1}) and operational stability, require high-temperature vacuum deposition. Gold nanoparticles have been utilized in printing highly conductive elements for TFTs,³ but the high cost of gold has overshadowed the attributes of this otherwise appealing approach.

Solution-processable silver materials have been investigated as an alternative approach to low-cost printable conductors.⁴ Silver pastes and inks generally provide low thin-film conductivity,^{4c} while commercial silver nanoparticles gave high conductivity for thin-film features (< 200 nm) only at high sintering temperature due to relatively large particle sizes or presence of strong stabilizers. Electroless plating of silver has been used with microcontact printing to fabricate TFT electrodes,^{4d} but this method appears to be too complex to be practical. Recently, we reported the design of amine- and acid-stabilized sub-10 nm silver nanoparticles which could be converted to highly conductive, functionally capable electrical conductors for TFTs.^{4a,b} However, the preparation of such silver nanoparticles for low-temperature coalescence to conductive elements remains relatively challenging synthetically. The low yields or poor stability of silver nanoparticles may lead to increased cost and potentially preclude their adoption in practical applications.

We describe here a simple solution process to silver conductor for low-cost printed electronics using a solution of a silver(I) salt (e.g., silver acetate), an organoamine (e.g., ethanolamine), and a long-chain carboxylic acid (e.g., oleic acid) in an alcohol solvent (e.g., *n*-butanol). The solution was first deposited as a thin film on a substrate via various solution techniques (e.g., coating, stamping, printing, etc.), and then thermally converted directly to conductive elements without going through a silver nanoparticle intermediate. Although silver salts are known to thermally self-reduce to metallic silver, such reduction generally requires a high temperature.⁶ Strong reducing agents, such as NaBH_4 , hydrazine, and aldehyde, on the other hand, would cause rapid reduction of silver salt solution, leading to uncontrolled precipitation. Since both organoamine and alcohol are mild reducing agents for silver salts,⁷ we therefore utilized a low molecular weight hydroxy-substituted alkylamine for

Scheme 1

reduction of Ag(I) to Ag(0) . The complexation of the amine function of hydroxyalkylamine to Ag(I) would ensure its availability for reduction during annealing, while its low molecular weight would enable its facile evaporation off the silver film after reduction.

We found that addition of a carboxylic acid to the silver salt solution improved the continuity of the resulting silver film, leading to significantly increased conductivity. Specifically, a spin-coated, clear silver acetate/ethanolamine film on a glass substrate gave a silver film with a conductivity of about 1.0 – 2.0×10^3 S cm^{-1} on annealing in air at 200 °C for 10 min. On the other hand, a similar silver salt film provided a significantly higher conductivity of 1.0 – 2.0×10^4 S cm^{-1} under similar annealing conditions when a small amount of oleic acid was added to the solution. Figure 1 shows the conductivity of the resulting silver film as a function of chain length of the aliphatic carboxylic acid additive. The conductivity increased dramatically from a chain length of 7 to about 10 carbon atoms and then leveled off—an increase in conductivity of as much as 1 order of magnitude was observed. A high conductivity ($> 10^4$ S cm^{-1}) could also be achieved at a lower annealing temperature of 150 °C given sufficient annealing time (~ 45 min). The resulting silver films showed good adhesion on glass and silicon wafer substrates.

The effects of acid additive could be understood by studying the surface morphology of resultant silver film using optical microscopy. With no acid or an acid additive of a shorter chain length ($\leq \text{C}_7$), the resultant silver film contained numerous crystalline domains (Figure 1, inset a) whose boundaries were believed

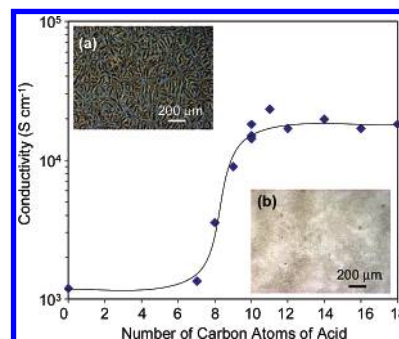


Figure 1. Conductivity of resultant silver film as a function of chain length of the carboxylic acid additive. Insets: optical images of resultant silver films from silver salt solution with (a) no acid additive showing numerous crystalline domains and (b) oleic acid additive showing homogeneous film.

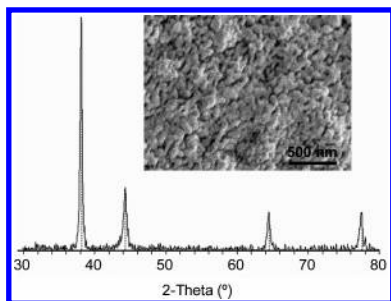


Figure 2. Thin-film X-ray diffraction of a silver salt solution annealed at 150 °C for 45 min. Inset is a SEM image of the resulting silver thin film.

to impede electrical conduction in the film, thus lower electrical conductivity. With a longer carboxylic acid additive ($>C_8$), a homogeneous thin film with no discernible crystalline domain boundaries was formed (Figure 1, inset b), thus the observed higher electrical conductivity. Shorter-chain acids showed no effects since they were too volatile and would be evaporated off during annealing. Longer-chain acids slowed down on silver crystallization, leading to a more homogeneous silver film containing less but larger crystalline domains.

Highly conductive silver thin films prepared by this approach were further characterized using X-ray and SEM analyses (Figure 2). X-ray diffraction displayed diffraction peaks at $2\theta = 38.10$, 44.20 , 64.34 , and 77.39° , which were identical to those of a vacuum-deposited silver film.⁸ SEM image showed a continuous silver film of coalesced silver particles having an average particle size of 50–100 nm.

The performance of solution-processed silver conductors of the present approach was evaluated as the source/drain electrodes in a TFT device. Unlike single-layer conductive tracks such as antennas for RFID tags or conductive lines for electronic interconnects, a multilayered TFT structure would present a more challenging environment for evaluating the functional performance of conductive elements. Poor interfacial contacts and/or intermixing of organic semiconductor with the silver electrodes during deposition and annealing would adversely affect the device performance. TFT devices of a bottom-gate, bottom-contact structural configuration were built on an n-doped silicon wafer using silver source/drain electrodes generated from the silver acetate solution and a channel semiconductor comprised of a spin-coated PQT-12 thin film.^{2a} All the experimental TFT devices exhibited excellent field-effect transistor (FET) characteristics, which conformed closely to the conventional gradual channel model in both the linear and saturated regimes (Figure 3). The devices provided high FET mobility of $0.10\text{--}0.15\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, high current on/off ratio of 10^7 , close to zero turn-on voltage, and low threshold voltage of -6 V . These were similar to those of reference TFTs with vacuum-deposited gold electrodes^{2a} and were significantly superior to those of reference TFTs with vacuum-deposited silver electrodes (mobility of $\sim 0.06\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$; on/off ratio of $10^6\text{--}10^7$). No contact resistance was observed with smaller channel TFT devices ($\sim 20\text{ }\mu\text{m}$) even though it was present in similar devices with vacuum-deposited silver source/drain electrodes. The absence of contact resistance is believed to be due to the doping of PQT-12 semiconductor at the electrode/semiconductor interface by the residual carboxylic acid on the surface of the resultant silver electrodes.^{4b}

This approach is particularly significant for flexible electronics in that the formation of metallic silver could be accomplished at a

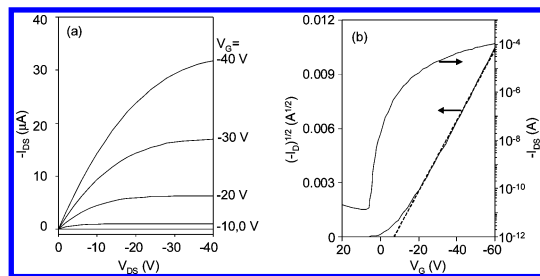


Figure 3. (a) Drain current I_{DS} versus source/drain voltage V_{DS} as a function of gate voltage V_G for an illustrative TFT with silver source/drain electrodes from the silver salt solution (channel length and width are, respectively, 25 and $1340\text{ }\mu\text{m}$). (b) I_{DS} and $(-I_{DS})^{1/2}$ versus V_G at a constant $V_{DS} = -60\text{ V}$ used for calculation of the mobility and current on/off ratio.

relatively low temperature which is compatible with the structural and dimensional integrity of commercial plastic substrates. The silver acetate/hydroxylamine/carboxylic acid/*n*-butanol solution used for the preparation of the silver conductor was very stable at room temperature in the dark as no precipitation in the solution was observed after being stored for over 6 months.

In conclusion, we have developed a simple approach to a printable silver conductor for microelectronics. Our silver conductive features exhibited high electrical conductivity similar to that of a vacuum-deposited silver conductor, yet worked far more efficiently as electrodes in TFTs.

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Supporting Information Available: Instrumentation, silver precursor formulation, device fabrication. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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