

Printed Silver Ohmic Contacts for High-Mobility Organic Thin-Film Transistors

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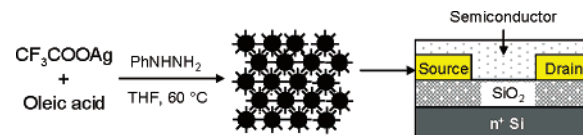
Organic thin-film transistors (OTFTs) have attracted great interest as low-cost alternatives to their silicon counterparts for large-area, flexible, and ultralow-cost electronics.¹ Most research efforts in this area over the past decade have been primarily devoted to liquid processable semiconductors,² while studies of conductive materials for printing equally important electrical conductors are of relative recent nature.^{3–5} Printable materials which possess sufficiently high electrical conductivities and energetic compatibility with semiconductors are required for printing low-cost OTFT circuits. Earlier works on printable conductive materials have largely focused 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. Recently, gold nanoparticle dispersions have been utilized in printing highly conductive elements,³ which function satisfactorily as electrodes in OTFTs. However, the high cost of gold has overshadowed the attributes of this otherwise appealing approach for low-cost electronic applications.

Not surprisingly, silver nanoparticles have received increasing attention as potentially much lower-cost alternatives,⁴ but for OTFTs using p-type semiconductors, such as regioregular polythiophenes, silver electrodes are energetically incompatible. Our studies showed that polythiophene-based OTFTs with silver source/drain electrodes, both from vacuum deposition and silver nanoparticles, afforded significantly lower field-effect transistor (FET) mobilities.^{4a} This was a consequence of inefficient charge carrier injection caused by contact resistance often observed in OTFTs, which led to adversely impacted FET performance.⁶ Several attempts to modify electrode surface chemistry via for example alkanethiol self-assembled monolayers (SAMs) to enable better charge injection have met with varying degrees of success.^{6c,d}

In this communication, we describe a novel approach to resolving the energetic mismatch of silver electrode with regioregular polythiophene semiconductors via in situ modification of their interfacial properties to enable ohmic contact formation. The ability to use silver to satisfy all the conductor needs for polythiophene-based OTFT circuits is particularly important because (1) regioregular polythiophenes are currently one of the most promising classes of solution-processed semiconductors for OTFTs, and (2) it would be far more cost-effective and desirable if only one type of printable conductor is used throughout.

The rationale for this approach was based on the following considerations: (1) our recent results showed that some stabilizers or their thermally transformed entities remained on the surface of annealed silver nanoparticle films since the latter exhibited larger advancing water contact angles than those from vacuum deposition; (2) regioregular polythiophene OTFTs with PEDOT/PSS-coated copper source/drain electrodes provided significantly higher mobility than those with untreated copper electrodes (see Supporting Information); and (3) if the stabilizer of silver nanoparticles had

Scheme 1



the ability to dope polythiophenes in much the same manner as PSS to PEDOT, then the annealed silver electrodes from these silver nanoparticles would be rendered energetically compatible with polythiophene semiconductors. Since carboxylic acids can readily dope polythiophenes and increase their conductivity, the carboxylic acid-stabilized silver nanoparticles such as those stabilized with oleic acid would represent ideal precursors for this purpose.

Oleic acid-stabilized silver nanoparticles were previously prepared in low yields via a high-temperature synthesis.⁷ We developed a more efficient synthesis using an organic hydrazine to convert silver trifluoroacetate to oleic acid-stabilized silver nanoparticles under mild reaction conditions. Specifically, the preparation involved addition of 0.55 mol equiv of phenylhydrazine into a solution of 1 mol equiv of silver trifluoroacetate containing 7.5 mol equiv of oleic acid in THF, followed by reaction at 60 °C for 20 min (Scheme 1). A follow-up simple workup yielded silver nanoparticles in about 60% yield. These silver nanoparticles were easily dispersible in common organic solvents such as hexane, toluene, THF, etc. The TEM image showed that they were almost monodispersed with a mean particle size of ~6 nm (Figure 1a). This narrow particle size distribution would be expected to enable facile self-assembly of these particles into close packing when printed, thus greatly facilitating their coalescence into a continuous conductive film.

To demonstrate formation of an electrically conductive element, the silver nanoparticles were first dispersed in cyclohexane at (5–10 wt %) and spun cast on a glass slide into a reddish brown thin film. When the latter was heated in air at 200 °C for about 30 min, a shining silver mirrorlike surface was formed. SEM image showed a continuous silver layer of coalesced silver particles with an average particle size of 50–100 nm (Figure 1b). X-ray diffraction displayed diffraction peaks at $2\theta = 38.1, 44.2, 64.34, \text{ and } 77.39^\circ$, which were identical to those of a vacuum-deposited silver film.⁸

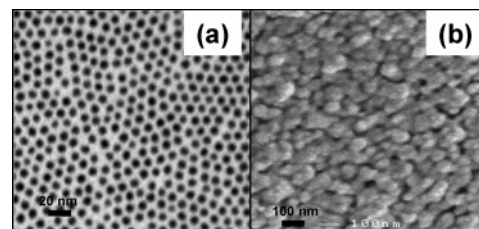


Figure 1. (a) TEM image of oleic acid stabilized silver nanoparticle; (b) SEM image of silver nanoparticles thin film after annealing.

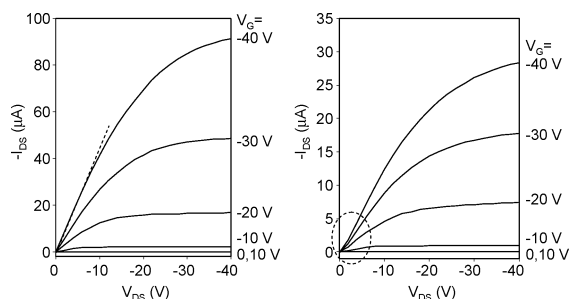


Figure 2. Plots of drain current I_{DS} vs source-drain voltage V_{DS} as a function of gate voltage V_G for exemplary OTFTs with source/drain electrodes fabricated from (a) oleic acid stabilized-Ag nanoparticles and (b) oleylamine stabilized-Ag nanoparticles (or vacuum deposition). The channel length and width are respectively 18 and 1600 μm .

The conductivity of the resulting silver thin film was in the range of $2\text{--}4 \times 10^4 \text{ S cm}^{-1}$, comparable to that of vacuum-deposited silver film with similar thickness ($4\text{--}6 \times 10^4 \text{ S cm}^{-1}$). The annealed silver film exhibited a water contact angle of 112° , indicative of a highly hydrophobic surface in contrast to that from vacuum deposition showing a contact angle of 54° . The contact angle of annealed silver film remained unchanged even after extensive washings with organic solvents such as hexane, toluene, and 2-propanol. These results suggested the presence of a layer of oleic acid or its chemically transformed derivative on the surface of annealed silver nanoparticle film. This is also supported by previous studies on annealing of gold nanoparticles, showing occurrence of stabilizers on the surface of enlarged gold particles.⁹

A series of bottom-contact OTFTs were fabricated on an n-doped silicon wafer with an octyltrichlorosilane-modified SiO_2 dielectric layer using a spun-cast poly(3,3''-didodecyl-quarterthiophene) semiconductor (PQT-12),^{2a,b} and silver source/drain electrodes printed from the present silver nanoparticles (see Supporting Information). For comparison, OTFTs with silver electrodes from printed oleylamine-stabilized silver nanoparticles and vacuum deposition were also prepared. With large channel lengths, such as about 90 μm , no contact resistance was observed in all three types of OTFTs even though significant differences in field-effect mobility were noted. The devices with electrodes printed from oleic acid-stabilized silver nanoparticles gave mobility of $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off ratio of 10^7 , which are identical to those of OTFTs with vacuum-deposited gold electrodes. In sharp contrast, the devices with silver electrodes fabricated by vacuum deposition or from oleylamine-stabilized silver nanoparticles gave a much lower mobility of $0.03\text{--}0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off ratio of 10^6 .

Using smaller channel lengths of $\sim 20 \mu\text{m}$, contact resistance arising from energetic mismatch could be directly observed in the output curves of OTFTs with silver electrodes from both vacuum deposition and oleylamine-stabilized silver nanoparticles. A characteristic S-shaped curve typifying of presence of contact resistance was evident in the linear regimes of the output curves of these devices (Figure 2b). On the other hand, the OTFTs with silver electrodes printed from oleic acid-stabilized silver nanoparticles exhibited ideal ohmic contact characteristics: a linear current–voltage relationship at source-drain voltage $<$ gate voltage. These devices also displayed better saturation behaviors and much higher saturated currents.

The pronounced differences in performance of these OTFTs can be understood on the energetic considerations of these materials:

silver has a work function of $\sim 4.3 \text{ eV}$ which is significantly different from the HOMOs of regioregular polythiophenes ($\sim 4.9\text{--}5.2 \text{ eV}$) such as PQT-12. The pairing of normal silver electrode with PQT-12 would lead to a charge injection barrier, thus causing the observed lower carrier mobility. The presence of oleic acid or its chemically transformed species on the surface of electrodes fabricated from oleic acid-stabilized silver nanoparticles effectively doped the PQT-12 semiconductor at the electrode/semiconductor interface, enabling establishment of ohmic contact and hence efficient charge carrier injection. On the other hand, oleylamine or its chemically transformed derivative left on the annealed oleylamine-stabilized silver nanoparticle electrodes was incapable of doping the electron-rich regioregular polythiophene, thus the occurrence of contact resistance.

In summary, we have demonstrated that carboxylic acid-stabilized silver nanoparticles represent ideal printable precursors to highly conductive elements for use in low-cost printed OTFT circuits. The contact resistance typically observed with silver electrodes in polythiophene OTFTs can be eliminated with the silver electrodes printed from carboxylic acid-stabilized silver nanoparticles.

Acknowledgment. Partial financial support of this work is provided by the National Institute of Standards and Technology through an Advanced Technology Grant (70NANB0H3033).

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

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JA058725W