

Investigation of charge injection in organic thin film transistor using ink-jet printed silver electrodes

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Abstract

We fabricated a coplanar type organic thin-film transistors using ink-jet printed silver source/drain electrodes and α,ω -dihexylquaterthiophene (DH4T) which is an active layer. Use of ink-jet printed silver nanoparticle-based metal electrode assists the energetic mismatch with p-type organic semiconductor via modification of their interfacial properties to enable ohmic contact formation.

1. Introduction

Organic thin-film transistors (OTFTs) has recently received great attention because of their potential applications in flexible, low-cost integrated circuit such as smart cards and radio frequency identification (RFID) tags, display backplanes such as liquid crystal displays and electronic paper, and organic electroluminescent displays [1,2]. Furthermore, the possibility of using low-cost solution or liquid fabrication techniques has fuelled the current surge in research interest in organic electronics. So far, most conductive materials that have been utilized as an electrode in the OTFT are metals such as gold. They are typically deposited by vacuum evaporation through a shadow mask or via vacuum deposition of the metal onto the substrate, followed by photolithographic patterning. However, these deposition methods are not only time consuming but also very complicated and expensive, as many steps are required to construct one layer of a pattern. On the other hand, solution-processable conductive materials such as poly(3,4-ethylenedioxythiophene/poly(styrenesulfonate) (PEDOT / PSS) and doped polyaniline possess relatively low conductivities and poor operational stability [3,4]. To satisfy these manufacturing cost and device performance issues, we introduced the ink-jet printing technique to fabricate metallic source and drain electrodes.

Silver nanoparticles have received increasing attention as potentially much lower-cost alternatives,

but for OTFTs using p-type semiconductors, such as thiophene derivatives, silver electrodes are energetically incompatible [5-6]. Our studies also shows that thiophenes-based OTFTs with vacuum deposited silver source/drain electrodes exhibits significantly lower field-effect transistor (FET) mobility. This was a consequence of inefficient charge carrier injection caused by contact resistance often observed in OTFTs. 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 [7]. In our research, we fabricated a coplanar type OTFTs using ink-jet printed silver source/drain electrodes and α,ω -dihexylquarter thiophene (DH4T) which is an active layer. Use of ink-jet printed silver nanoparticle-based metal electrode assists the energetic mismatch with p-type organic semiconductor.

2. Experimental

Silver nanoparticles of about 20 nm size were synthesized in our laboratory by the polyol method and used as conductive materials for ink [8]. The viscosity of the inks was ~ 5.6 mPa·s at a shear rate of 50 s⁻¹, as measured by a cone and plate viscometer (DV-III+, Brookfield Engineering) and the surface tension of the inks was 39 mN/m (DST30, SEO) [9]. The conductive ink was printed by an ink-jet printer onto the heavily doped n-type silicon wafer with 200-nm thick thermal SiO₂ layer as a substrate. The printer set up consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured by Microfab Technologies, Inc. (Plano, TX) and the diameter of orifice was 30 μ m. The ink-jetted electrodes were heat-treated at 200 °C for 30 min in order to develop the conductive path by particles sintering. α,ω -dihexylquaterthiophene (DH4T) dissolved in a chlorobenzene as an active material of organic semiconductor was then deposited between the ink-jet

printed silver electrodes by drop-casting. For comparing between the devices with ink-jet printed silver electrodes and the one with vacuum deposited electrodes, we fabricated the devices with 49-nm thick silver electrodes deposited onto the heavily doped n-type silicon wafer with 200-nm thick thermal SiO₂ layer using a thermal evaporator. The 1-nm thick chromium was pre-deposited for improvement of adhesion between electrodes and SiO₂.

3. Results and discussion

Fig. 1 shows UV photoemission spectroscopy (UPS) results for two different electrodes: ink-jet printed and vacuum deposited silver films. UPS data show an increase in work function for the ink-jet printed silver film. The work function of ink-jet printed silver film was 4.7 eV, while that of vacuum deposited silver films was 4.2 eV, which is close to the reported value for pure Ag.

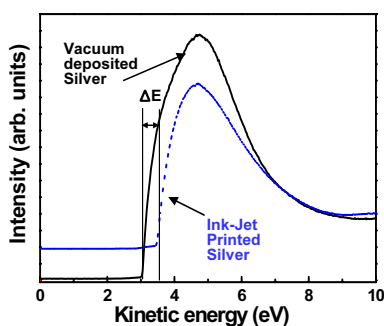


Fig. 1. UV photoemission spectroscopy data of vacuum deposited and ink-jet printed silver film

Chemical modification schemes are of interest to tailor the effective work function of metal to control energetic barriers to charge injection. Self-assembled monolayers (SAMs) of thiols on metal surfaces are one approach to tuning the work function with different terminal functional groups [7]. This was induced by surface modifiers with both positive and negative dipoles and metal/organic contacts can be controlled. Similar studies using covalently bonded surface modifiers on metal surfaces suggest that a wide degree of control of effective surface work function is possible. For the silver, the other hand, the chemisorption of oxygen on silver surface usually increases the work function at the magnitude of 0.6 – 1.0 eV because the chemisorbed oxygen atoms capture electrons from the underlying Ag atoms [10]. It is likely that the Ag nanoparticles are covered by

poly(N-vinyl-2-pyrrolidone) (PVP), which was added as a dispersant during the synthesis and PVP is still present intact even after the annealing at 200°C. The oxygen present in the PVP functional group can chemisorb on the Ag. To understand the increase in work function and its influence on the device performance, a detailed surface chemical analysis is necessary.

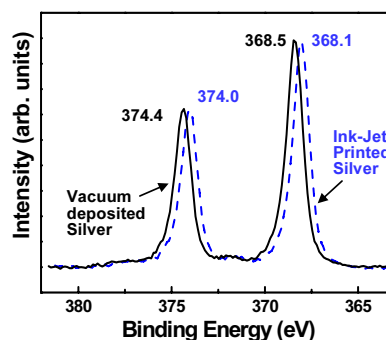


Fig. 2. X-ray photoemission spectra of vacuum deposited and ink-jet printed silver film

Fig. 2. shows high-resolution XPS result of Ag 3d elements for the two silver films. XPS spectra for Ag are very sensitive to the chemical environment around the silver atoms, particularly to the electron-donating ability of the organic ligand and to the strength of the interaction between silver and the organic ligand. The peak was shifted toward a lower binding energy. This indicates that the surface chemistry of the ink-jet printed Ag was different compared to the evaporated Ag. The adsorption of the oxygen atom in C=O on the silver particle can induce an image dipole on the particle surface, that is, partially positive charges present on the surface of the ink-jet printed silver.

Fig. 3. shows output and transfer characteristics of the OTFT devices with the ink-jet printed silver source and drain electrodes and the vacuum deposited silver electrodes. The channel width and length ratios (W/L) are 3000/210 μm for the ink-jet printed electrode and 3000/80 μm for the vacuum deposited electrode. Transfer characteristics were measured at a constant V_D = -30 V.

The OTFT device with the ink-jet printed electrodes exhibited excellent field-effect transistor characteristics, which conformed well to the conventional gradual channel model in both the linear and saturated regimes. The output curve shows good saturation behavior and no significant contact resistance. This device showed a mobility of $1.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the saturation regime, and on/off current

ratio over 3×10^3 and a threshold voltage of about -13 V with subthreshold slopes of ~ 3 V dec⁻¹. On the other hand, the OTFT devices with vacuum deposited silver source and drain electrodes shows very poor electrical performance. The parameters of the vacuum deposited devices are a mobility of 9.1×10^{-5} cm² V⁻¹ s⁻¹ in the saturation regime, and on/off current ratio over 6×10^2 and a threshold voltage of about -5 V. Furthermore, the output curve shows very unstable and low on-current value compared to the device with ink-jet printed electrodes, even though the device with vacuum deposited electrodes has higher W/L ratio.

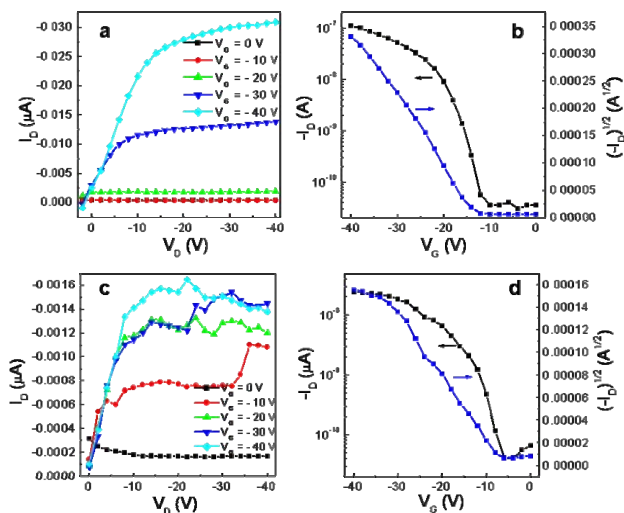


Fig. 3. Output and transfer characteristics of the OTFT devices with (a)/(b) the ink-jet printed silver source and drain electrodes; (c)/(d) the vacuum deposited silver electrodes.

Differences in electrical performances of these OTFTs can be explained by the energetic alignment and the work function of the source/drain electrodes. In the case of vacuum deposited silver electrodes, the work function is 4.2 eV, which is significantly different from ionization energy of regioregular polythiophenes ($\sim 4.9 - 5.2$ eV) such as DH4T [5-7]. The mismatching of the work function between the evaporated silver electrode and DH4T would lead to a charge injection barrier, which can cause lower carrier mobility as in our experiment. On the other hand, better device performance with a lower contact resistance associated with the OTFT fabricated by the ink-jet printed silver electrodes, which has work function of 4.7 eV, may indicate that the printed electrode is energetically compatible with the organic semiconductor such that ohmic contact can be

established to allow efficient charge injection. As a result, the ink-jet printed silver can be used as an electrode for OTFTs, even though pure silver is energetically mismatched.

4. Summary

In our research, we fabricated a coplanar type OTFTs using ink-jet printed silver source/drain electrodes and α,ω -dihexylquaterthiophene (DH4T) which is an active layer. Ink-jet printing of silver nanoparticles helps the energetic mismatch of silver electrode with p-type organic semiconductor via modification of their interfacial properties to enable ohmic contact formation. Several research have been demonstrated the improved interfacial contacts between active layer and solution processable particulate metallic electrodes, but most of them shows experimental results of electrical performances. In this report, we suggested possible explanation for better device characteristics of the transistors based on the ink-jet printed Ag. Surface chemical analysis in conjunction with the work function measurement provides us better understanding of the energetic mismatch issue and the mechanism for work function modification.

5. References

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