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Organic thin film transistor using silver electrodes by the ink-jet printing technology

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Abstract

We have developed a conductive ink containing silver nanoparticles from which the electrodes for organic thin film transistor were directly patterned by ink-jet printing. Nano-sized silver particles having ~20 nm diameter was used for a direct metal printing. Silver conductive ink was printed on the heavily doped n-type silicon wafer with 200-nm thick thermal SiO_2 layer as a substrate. To achieve a high line resolution and smooth conductive path, the printing conditions such as the inter-drop distance, stage moving velocity and temperature of the pre-heated substrates were optimized. After the heat-treatment at temperatures of 200 °C for 30 min, the printed silver patterns exhibit metal-like appearance and the conductivity. To fabricate a coplanar type TFTs, an active material of semiconducting oligomer, α,ω-dihexylquaterthiophene (DH4T) in a chlorobenzene was deposited between the ink-jet printed silver electrodes by drop casting. The OTFT with the ink-jetted source/drain electrodes shows general performance characteristics with good saturation behavior and no significant contact resistance as compared to the one with vacuum deposited electrodes. The electrical characteristic parameters of OTFT show the mobility of 1.3×10^{-3} cm^2 V^{-1} s^{-1} in the saturation regime, on/off current ratio over 10^3, and threshold voltage of about −13 V.

Keywords: Organic thin film transistors; Ink-jet printing; Conductive pattern; Silver nanoparticles

1. Introduction

In the electronic industry, fabrication of conductive tracks is inevitable. Conventional photolithographic and electroless deposition techniques are widely adopted in the printing circuit board (PCB) for manufacturing its conductive circuits. However, this method is not only time consuming but also very complicated and expensive, because many processing steps are required to construct a layer of the circuit. Moreover, the electroplating and etching processes also produce large quantities of chemical waste. Therefore, there is an industrial need for direct digital printing to simplify the processes and to reduce manufacturing costs [1,2].

Ink-jet printing is a particularly attractive technique, for a direct write of patterns and the delivery of precise quantities of materials. Recent years have been growing efforts to explore new possibilities in the field of microdispensing in materials assembly in the electronic and display industries, beyond conventional image transfer capabilities [3,4]. In particular, it is desirable to fabricate onto polymeric or similar temperature-sensitive substrates by solution-based printing process [1,5]. Development of a solution-based process on a flexible substrate would allow roll-to-roll fabrication, which is an extremely inexpensive way to mass-produce circuits since it eliminates conventional photolithography and complex substrate processing including vapor phase deposition and etching. For these reasons, the ink-jet printing as a convenient and rapid processing technique to fabricate conductive lines has attracted great attention in recent years [6–11].

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 [12]. The possibility of using low-cost solution or liquid fabrication techniques has fuelled the current surge in research interest in organic electronics [13–18]. Most of the works have however focused on the development of solution processable organic semiconductors. Other OTFT

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components such as solution processable conductor and dielectric materials have not been receiving much attention, despite their critical roles in the OTFTs. The conductor materials of electrodes are particularly important as they have decisive impacts on the electrical properties. They have to meet requirements such as ohmic contact formation with the organic semiconductor layer for efficient charge carrier injection, chemical inertness toward the semiconductor and dielectric layers, and sufficient operational stability to withstand the stress of the applied voltage and generated current [12]. Furthermore, for applications in flexible electronics such as e-paper, the conductors should also be fabricated at a reasonably low temperature that is compatible with the flexible substrate materials such as plastic films [1].

In this work, we demonstrated the fabrication of a coplanar type OTFTs using ink-jet printed silver source/drain electrodes. The conductive ink containing silver nanoparticles was ink-jet printed onto heavily doped n-type silicon wafer with thermal SiO_2 layer, which act as common gate electrode and dielectric. Semiconducting oligomer α,ω-dihexylquaterthiophene (DH4T), was drop cast between the ink-jet printed source/drain. The device characteristics of the OTFTs involving the printed electrode were compared to the one with evaporated electrode.

2. Experimental

The silver nanoparticles were synthesized by the well-known polyol method [19,20]. Silver nitrate (99.9%, Aldrich) used as a precursor of silver nanoparticles was dissolved in polyol medium. This solution was stirred vigorously in a reactor with a reflux condenser, followed by nucleation and growth reactions. After the reaction completes, the solution was cooled to room temperature, and the silver particles were separated from liquid by centrifugation and repeatedly washed with ethanol. The synthesized silver nanoparticles were dispersed in a mixed solvent of water and ethylene glycol. The formulated ink was ball milled for 24 h, followed by filtration through a 5 μm nylon mesh prior to the printing. The solid loading of the silver conductive ink was 20 wt.%.

The conductive ink was printed by an ink-jet printer onto the heavily doped n-type silicon wafer with 200-nm thick thermal SiO_2 layer as a substrate. The printer set up consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured from Microfab Technologies, Inc. (Plano, TX) and the diameter of orifice was 30 μm. The print head was mounted onto a computer-controlled three-axis gantry system capable of movement accuracy of ±5 μm. The gap between the nozzle and the surfaces was maintained at about 0.5 mm during printing. The uniform ejection of the droplets was performed by applying ~35 V impulse lasting ~20 μs at a frequency of 400 Hz. 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. Fig. 1 shows the schematic illustration of the fabricated OTFT device based on the ink-jet printed silver source and drain together with drop-cast DH4T. For comparison between the devices with ink-jet printed silver electrodes and traditional vacuum deposited electrodes, we fabricated the device with silver electrodes which was deposited onto the heavily doped n-type silicon wafer with 200-nm thick thermal SiO_2 layer using thermal evaporator. The evaporated film thickness was 50 nm.

The shape and size of the synthesized silver nanoparticles were observed using scanning electron microscopy (SEM, JSM-6500F, JEOL), and the particle size distribution was obtained by image analysis. The surface morphology and structure of the fabricated device were observed by optical microscopy (Leica, DMLM) and confocal laser scanning microscopy (LSM 5 Pascal, Carl Zeiss). The resistivity was calculated from sheet resistance which was measured by 4-point probe (CMT-SR200N, Chang Min Co., Ltd.) and the thickness of the printed Ag films which was obtained by SEM observation. The I–V measurements were performed in air using Agilent 5263A source-measure unit.

3. Results and discussion

3.1. Silver nanoparticle ink preparation

Fig. 2 shows the SEM image and the X-ray diffraction pattern of the synthesized silver nanoparticles. The mean

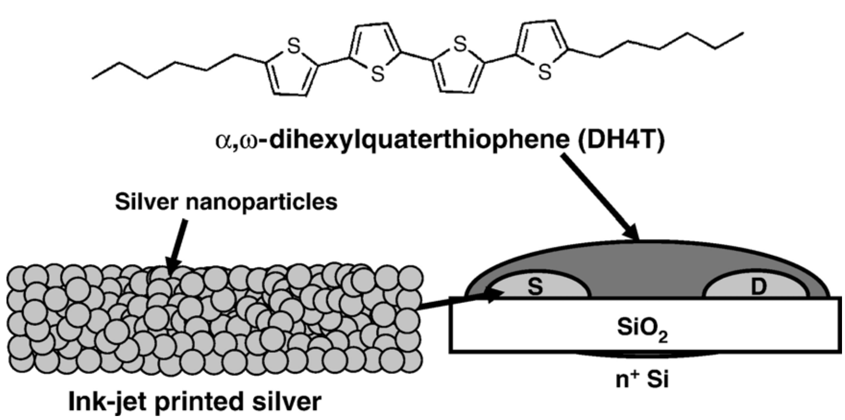

Fig. 1. Schematic depiction of the fabricated OTFT based on ink-jet printed silver source and drain with DH4T semiconducting layer.

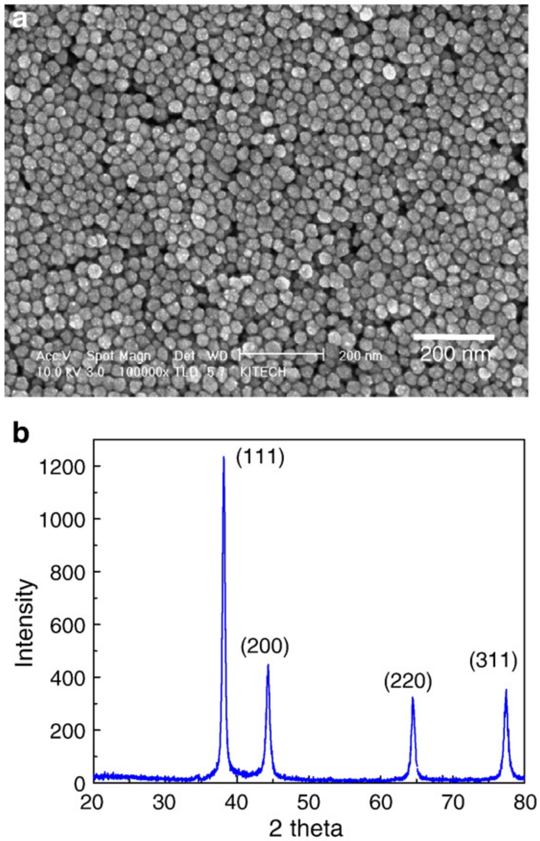

Fig. 2. (a) SEM image and (b) XRD of the synthesized silver nanoparticles for conductive ink.

size and size distribution of silver nanoparticles was determined to be 21±4 nm showing a relatively good monodispersity, as observed by SEM image (Fig. 2a). The X-ray diffraction pattern confirmed that the synthesized silver particles have peak characteristics of metallic pure silver with a good crystallinity without any impurity phase as presented in Fig. 2, even though they were synthesized at low temperature.

The mixture of water and ethylene glycol was used as the solvent for the inks to prevent formation of a coffee-ring shaped deposition in the printed patterns [21]. Dispersion stability of the prepared conductive silver inks was excellent. Inks exhibit nearly Newtonian rheological behavior. The viscosity of the silver conductive ink was about 3 mPa s at shear rate of 100 s^{-1} as measured by cone and plate viscometer and the surface tension of the ink was 30–40 mN/m. The conductivity of the ink-jet printed silver films has been investigated in our previous work [22]. The conductivity gradually increased with the increasing heat-treatment temperature and then reached nearly constant value when heat-treated at above 200 °C. The resistivity of Ag films at 200 °C was only four times larger than silver bulk resistivity of 1.62 μΩ cm. The ability to achieve such a high conductivity at lower sintering temperature resulted from reduced particle size to nanoscale [23–25], which is critical to be utilized on a plastic substrate for flexible electronics.

3.2. Fabrication of organic thin film transistor

To fabricate the coplanar type TFT, the prepared silver conductive ink was printed on heavily doped n-type Si wafer with 200-nm thick thermal SiO_2 layer, using a piezoelectric DOD ink-jet printing device. The 3D image and microstructure of ink-jet printed electrodes are presented in Fig. 3. Printed source and drain electrodes exhibited smooth edge structure in which the line-width of the electrode was about 200 μm. After the heat-treatment at temperature at 200 °C for 30 min, the printed silver patterns exhibit metal-like appearance and the conductivity of about 6.5 μΩ cm. The surface roughness of the printed silver electrodes was also observed by confocal laser scanning microscopy and RMS (root-meat-square) value was ~79 nm.

Fig. 4 shows the top view of the fabricated OTFT device based on ink-jet printed silver source and drain with drop-cast DH4T. The device has a channel width (W) of 3000 μm and a channel length (L) of 210 μm (W/L ratio = 14). For comparison, the OTFT with silver electrodes from vacuum deposition were also prepared. The device structure was identical to the one with the ink-jet printed electrodes except for channel width and length (W/L ratio = 37).

All measurements of the electrical characteristics of the devices were carried out in a metal black box. The effective

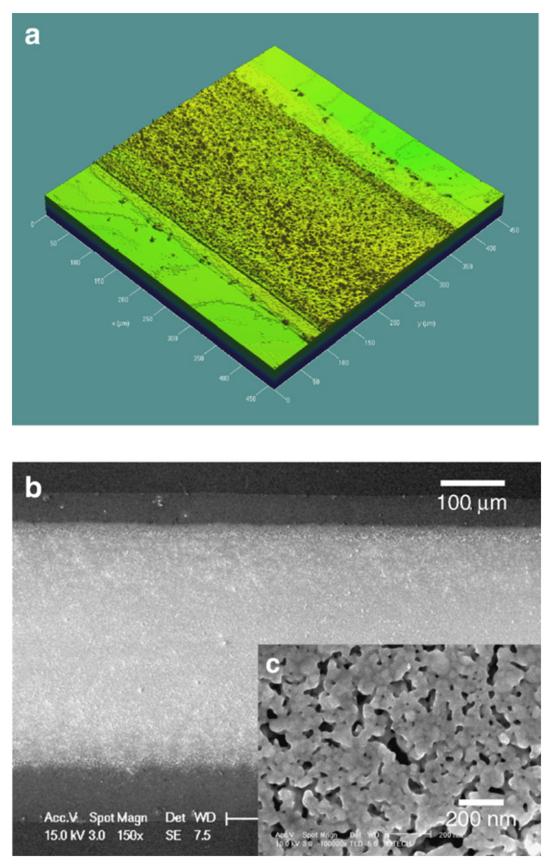

Fig. 3. Structures of the ink-jet printed silver electrode after heat-treatment at 200 °C for 30 min: (a) 3D image of confocal laser scanning microscopy; (b) SEM image of the ink-jet printed silver electrode; and (c) microstructure of the electrode.

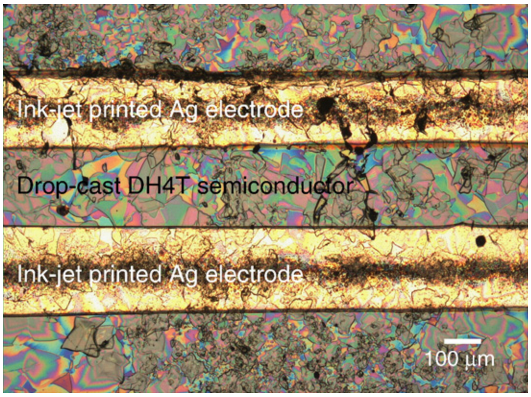

Fig. 4. Optical microscopy image of the top view of the fabricated OTFT with ink-jet printed silver electrodes and drop-cast DH4T.

mobility, μ_{eff}, was estimated in the saturation region as follows:

$$I_{\text{D}} = \frac{1}{2}\mu_{\text{eff}} C_{\text{i}} \frac{W}{L} (V_{\text{G}} - V_{\text{T}})^2 \quad (1)$$

where I_{D} is the drain current density, W and L are the channel width and length, respectively, C_{i} is the insulator capacitance, and V_{G} and V_{T} are the gate and threshold voltage, respectively.

Fig. 5 shows the output and transfer characteristics of the fabricated devices. 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 (Fig. 5a and b). The output curve shows good saturation behavior and no significant contact resistance. This device showed a mobility of 1.3×10^{-3} cm^2 V^{-1} 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 (Fig. 5c and d). The parameters of the vacuum deposited devices are a mobility of 9.1×10^{-5} cm^2 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 with the device with ink-jet printed electrodes, even though the device with vacuum deposited electrodes has higher W/L ratio.

Differences in electrical performances of these OTFTs can be explained by the energetic alignment and the work function of the source/drain electrodes. In general, silver has a work function of $\sim$4.3 eV, which is significantly different from ionization energy of regioregular polythiophenes (4.9–5.2 eV) such as DH4T [26–28]. 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

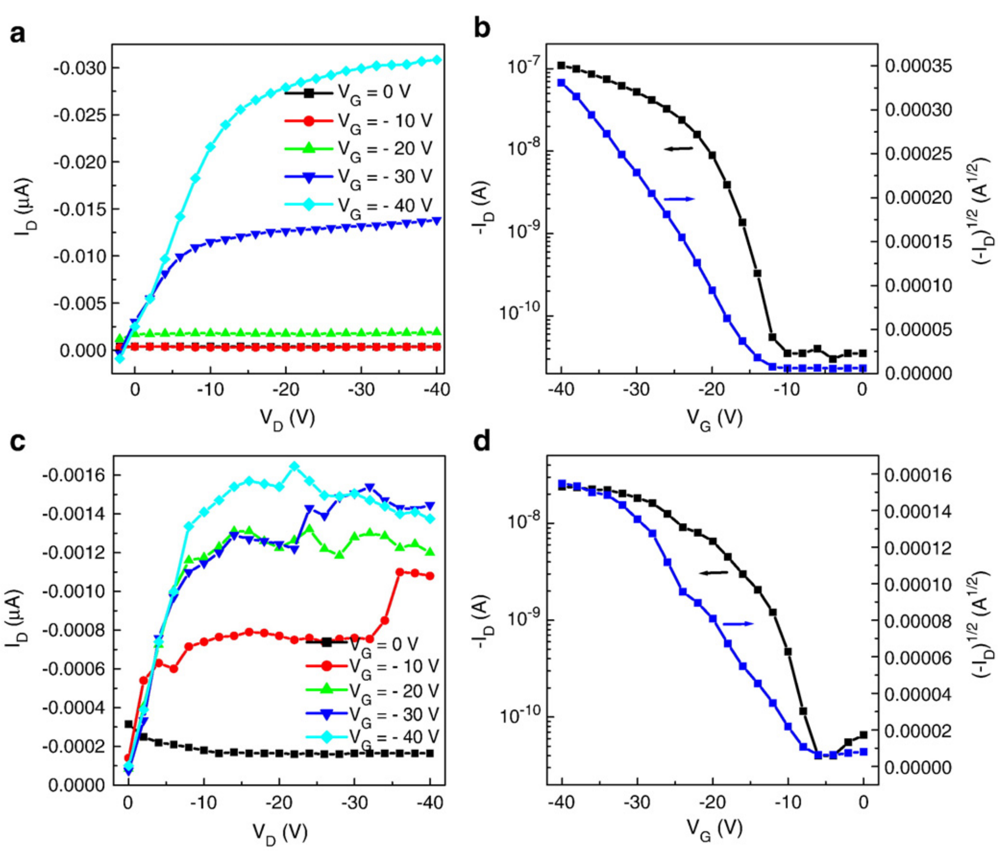

Fig. 5. Output and transfer characteristics of the OTFT devices with (a)/(b) the ink-jet printed silver source and drain electrodes; (c)/(d) the vacuum deposited silver electrodes. The channel width and length ratios (W/L) are 3000 μm/210 μm for the ink-jet printed electrode and 3000 μm/80 μm for the vacuum deposited electrode. Transfer characteristics were measured at a constant $V_{\text{D}} = -30$ V.

performance with nearly zero contact resistance associated with the OTFT fabricated by the ink-jet printing may indicate that the printed electrode is energetically compatible with the organic semiconductor layer such that ohmic contact can be established to allow efficient charge injection. The silver nanoparticles are surrounded by the polymeric stabilizer to prevent the particles from agglomeration, which was added during the preparation of the conductive ink. Even the printed electrodes undergo heat-treatment, it is expected that the silver particles in the printed electrode contains to some extent polymeric species. It is speculated that these remaining polymer or its chemically transformed species on the surface of silver electrodes can reduce the work function mismatch between the printed silver electrode and the semiconducting organic DH4T, enabling the establishment of ohmic contact and efficient charge carrier injection at the interface. In-depth investigation of the energetic alignment at organic and metal interface is currently underway.

4. Conclusions

We fabricated the OTFT with ink-jet printed silver source and drain, combined with drop-cast semiconducting oligomer DH4T. Ink-jet printing technology was applied to the TFTs fabrication process in which the conductive track was directly patterned by ink-jet printing of nanoparticles. It is an attractive alternative to photolithography for direct patterning conductive lines owing to low-cost, low-waste and simple process. In addition, semiconducting layer was deposited by solution process of drop-casting, which can also be replaced by ink-jet printing. In contrast to the device with vacuum deposited electrodes, the OTFT device with the ink-jet printed electrodes exhibited excellent field-effect transistor characteristics with no significant contact resistance in which the mobility is 1.3×10^{-3} cm^2 V^{-1} s^{-1} in the saturation regime, on/off current ratio over 3×10^3, and a threshold voltage ~-13 V with subthreshold slopes of ~3 V dec^{-1}. The difference in electrical performances of these OTFTs could be explained in terms of energetic alignment between the electrode and semiconducting organic.

Acknowledgments

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