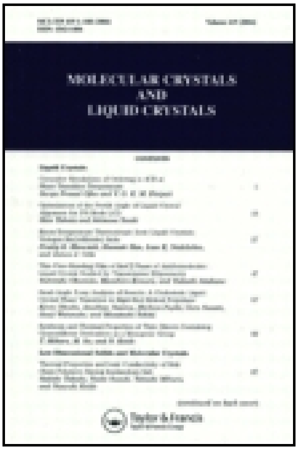

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Fabrication of the Organic Thin-Film Transistors Based on Ink-Jet Printed Silver Electrodes

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We present the organic thin-film transistors (OTFTs) based on the ink-jet printed silver electrodes as the source and drain electrodes. To fabricate the conductive silver electrodes by the low-temperature heat-treatment below 200°C, the inks containing silver nano-particles with the size of about 20 nm were printed on the silicon substrate with a 300 nm-thick SiO_2. It was observed that the conductivity of the ink-jet printed lines after heat-treatment at 200°C was similar to that of a bulk silver material. Poly(3,3″-dialkylquarterthiophene) (PQT-12) was deposited over the printed silver electrodes to fabricate the organic transistor. I–V character was measured to investigate an electrical performance of the fabricated transistor.

Keywords: ink-jet printing; nano-particle; organic thin-film transistors; silver

INTRODUCTION

Organic thin-film transistors (OTFTs) based on organic semiconductor have received great attention in the last decade because they were considered as potential alternative candidates to conventional inorganic TFTs in various applications including switching devices for active matrix liquid-crystal displays (AMLCDs), active matrix organic light-emitting diode displays (AMOLEDs), smart cards, electronic

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identification tags as well as sensing devices [1–4]. The performance of pentacene-based OTFTs has been close to that of amorphous silicon devices [5] and OTFTs can be achieved at low temperatures, providing large-area coverage even on plastic substrates. However, these OTFTs have been mainly fabricated by vacuum deposition and photolithographic patterning method so that the reduction in the manufacturing cost poses a major hurdle prior to its full exploitation. Therefore, the simple solution processes such as a coating or printing process to obtain the low-cost benefits have been recently researched. Besides the great advances that have developed the solution processable organic semiconductor with a superior performance, however, there has been relatively little works on the solution processable conductor which can be applied to the electrodes.

The conductor materials are particularly important as they have decisive impacts on the electrical properties. They need to meet specific electrical and materials requirements such as the ohmic contact with the organic semiconductor and high conductivity for an efficient charge injection. For large-area devices such as active matrix video displays, highly conductive electrodes are particularly critical in order to satisfy the fast switching rates. In addition, for application in flexible electronics, they should be also fabricated at low temperature where can be compatible with plastic substrate. The solution processable materials based on metals can satisfy these requirements, while the conducting polymer such as poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) and doped polyaniline possesses relatively low conductivity and poor operational stability [6,7].

We report here our researches of the synthesis of a silver metal nanoparticles and the preparation of the ink for ink-jet printing highly conductive electrodes of OTFTs. The conductivity of ink-jet printed electrode as a function of heat-treatment temperature is studied and the electrical characteristic of the organic thin-film transistors based on the ink-jet printed silver electrode is investigated.

EXPERIMENTAL

The silver nanoparticles were synthesized by a polyol method. Silver nitrate (99.9%, Aldrich) used as a precursor of Ag particles was dissolved in ethylene glycol (99.9%, Aldrich) and polyvinylpyrrolidone (Aldrich) was added to prevent agglomeration of the synthesized particles. This homogenous solution was stirred vigorously at 120°C for 30 min to induce the reduction reaction of a dissolved Ag ion. After a complete reaction, the solution was cooled at room temperature, and the synthesized particles were separated from the solution by a centrifugation method and the obtained particles were three times washed using an ethanol. To prepare the ink for ink-jet printing of conductive pattern, the synthesized silver nanoparticles were dispersed in a mixed solvent by ball-milling and ultra-sonication, followed by filtering through a 5 μm nylon mesh.

The dispersion stability of the prepared ink was excellent, representing the Newtonian rheological behavior and no sedimentation of silver nanoparticles was observed. The viscosity of the silver ink was $\sim$10 mP $\cdot$ s at shear rate of 50 s^{-1}, as measured by a cone and plate viscometer (DV-III +, Brookfield Engineering).

The Ag conductive ink was printed by an ink-jet printer onto the glass substrate to measure the conductivity of the printed silver pattern as a function of the heat-treatment temperature. The printer setup consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured from Microfab Technologies, Inc. (Plano, TX) with a 30-μm orifice. The print head was mounted onto a computer-controlled three-axis gantry system capable of a movement accuracy of $\pm$5 μm. The gap between the nozzle and the surfaces was maintained at 0.5 mm during printing at 25°C. The uniform ejection of the droplets was performed by applying 35 V impulse lasting 20 μS at a frequency of 200 Hz. A charge coupled device (CCD) camera equipped with a strobe light emitting diode (LED) light was employed to watch an individual droplet by which the physical properties of the droplets were analyzed. The resulting Ag conductive films were heat-treated in air on a hot plate from 70 to 300°C for 30 min at a constant heating rate of 5°C min^{-1}. The resistivity of heat-treated Ag films was measured by a four-point probe (Chang Min Co., Ltd., CMT-SR200N).

To fabricate bottom-contact OTFTs device, the silver conductive pattern was printed on heavily doped silicon substrate with 300 nm-thick silicon dioxide dielectric layer, followed by heat-treatment at 200°C. The width and length of channel are 3 mm and 100 μm, respectively. Then, poly(3,3″-dialkylquarterthiophene) (PQT-12, American Dye Source) as a semiconductor was deposited between the heat-treated silver electrodes by spin-coating a 0.3 wt% solution of PQT-12 in dichlorobezene. To investigate the electrical performance of the fabricated transistor, current-voltage characteristics was measured using Agilent 5263A in air and in the dark.

RESULTS AND DISCUSSION

Figure 1 shows silver nanoparticles with the size of about 20 nm synthesized by polyol process. It is observed that the synthesized silver nanoparticles are separated individually without forming the

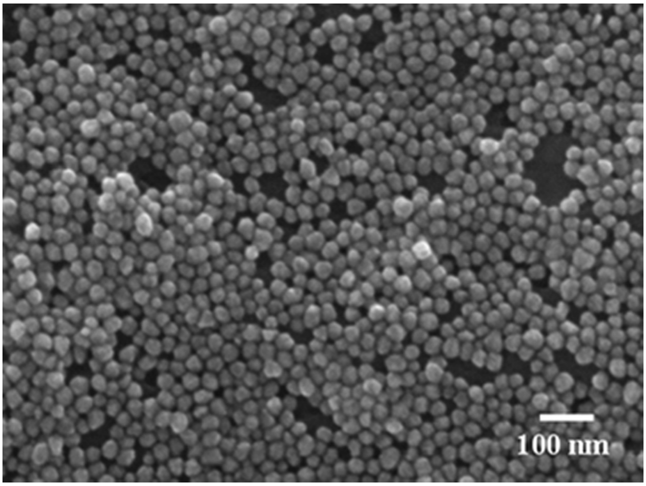


FIGURE 1 SEM image of the synthesized Ag monodisperse nanoparticle with the size of 20 nm.

agglomeration between particles. To obtain the highly conductive ink-jet printed film, the fabrication of well-packed particulate structure in the ink-jet printed film is critical, because the conductive path is formed via the connection between neighboring particles by sintering at low-temperatures. Therefore, the agglomeration between nanoparticles should be avoided to form the granular structure with high packing density. Such agglomeration-free particles can be achieved by controlling collision between initial nuclei during the particle synthesis. It is known that the agglomeration between particles in the polyol process can be minimized by the appropriate adsorption of protecting agent onto the particle surface, leading to the monodisperse nanoparticles [8]. In this respect, PVP was introduced as a protective agent.

Figure 2 shows the thermal properties of silver nanoparticles measured by thermogravimetric analysis (TGA). It is observed that the weight loss occurs in three temperature regions. The weight loss at the temperature below 150°C is due to the removal of the adsorbed water or remnant solvent, and the weight loss at the temperature above 150°C is attributed to the removal of capping molecules. However, because our capping molecule has polar group in carbon-hydrogen backbone, the different layer can be formed onto the silver nanoparticle. The inner layer was bound to the silver surface via specific interaction between silver nanoparticle and polar group of

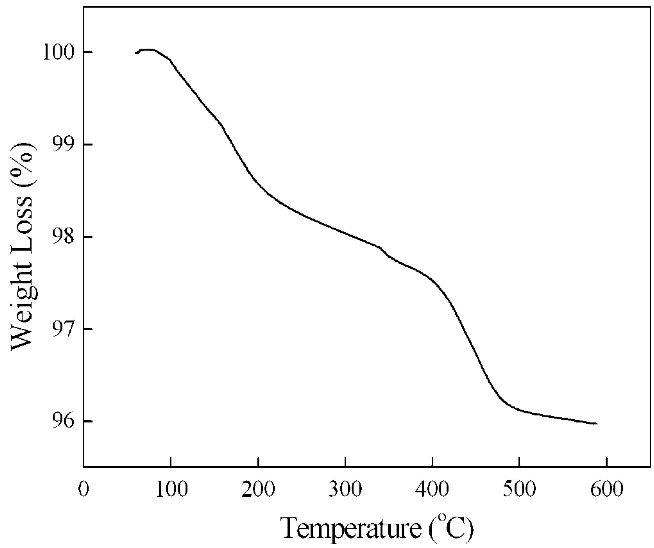
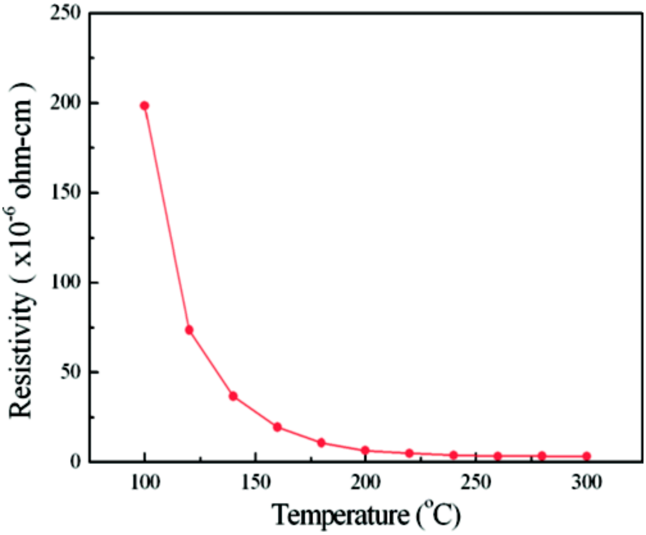


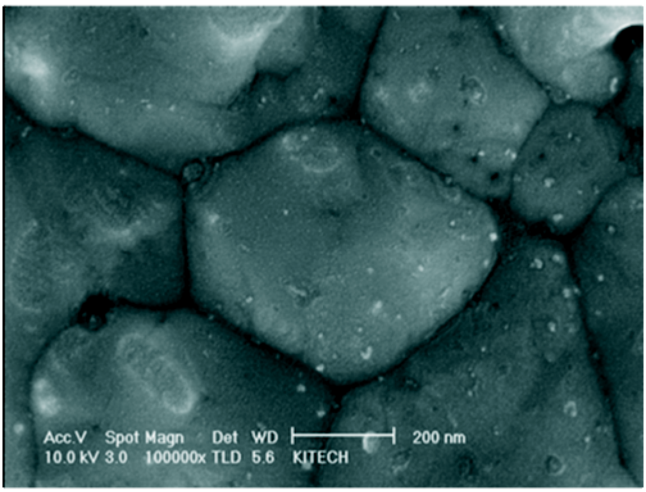
FIGURE 2 TG curves of the Ag particles used in the preparation of the conductive ink.

the capping molecule. The outer layer was composed of the capping molecule themselves attracted each other by van der Waals interaction. Accordingly, it is suggested that the two step weight loss at the temperature above 150°C results from the removal of the outer and inner layers, respectively.

Figure 3(a) shows 4-point probe measurement of silver film heat-treated at various temperatures. The resistivity decreases with increasing the heat-treatment temperature and it was saturated at the temperature above 275°C, exhibiting the similar resistivity compared with the silver bulk material. Before the heat-treatment, the silver nanoparticles were individually located in film, without formation of conductive path. With increasing the heat-treatment temperatures, the coalescence between particles occurs and the complete sintering between particles was accomplished at the temperature near melting-point, making the long-range conductive path. Because it can be assumed that the sintering temperature is about 80% of melting temperature, the sintering behavior is only observed at high temperatures ~800°C, considering the melting point of silver is 960°C. However, as the particle size is reduced to nanoscale, the melting temperature and sintering temperature can be significantly lowered and the sintering of silver nanoparticles with the size of about 20 nm can occur at 300°C as shown in Figure 3(b). In addition, the formation of conductive



(a)



(b)

FIGURE 3 Resistivity variations of the Ag conductive films composed of 20 nm silver nanoparticles as a function of heat-treatment temperatures and (b) SEM image for the microstructure of the Ag nanoparticle films heat-treated at 300°C.

path is related to another factor beside heat-treatment temperature. The capping molecule prevents the sintering between particles, because the sintering behavior is based on the diffusion of an atom and the capping molecules adsorbed onto the particle surface act as a

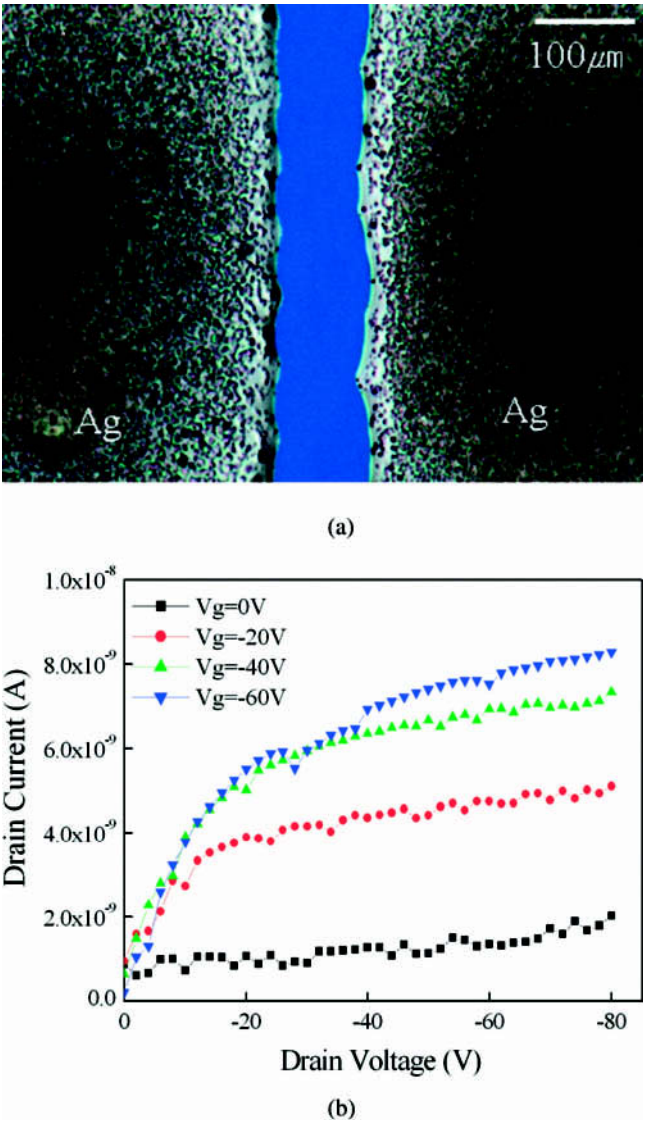


FIGURE 4 (a) Optical microscopy image of the silver electrodes printed onto the silicon dioxide layer (b) electrical performance of the transistor based on ink-jet printed silver electrode.

diffusion barrier. Therefore, the removal of capping molecules can accelerate the coalescence between nanoparticles and improve conductivity of the film containing silver nanoparticles. It is observed that the resistivity becomes quite low when the silver film was fired at the temperature at which the decomposition of capping molecule initiates.

The ink-jet printed silver electrode with the channel length of about 100 μm is shown in Figure 4(a) and the output characteristic of the fabricated OTFTs device is shown in Figure 4(b). It exhibits field-effect transistor characteristics, representing both the linear and saturated regimes. No noticeable contact resistance was observed in the experimental devices, though there is an energy barrier for the hole injection between silver electrode and PQT-12. (The work function of silver is 4.7 eV and HOMO (highest occupied molecular orbital.) energy level for PQT-12 is 5.2 eV). It can be suggested that the work function of the ink-jet printed silver electrode increases by capping molecules adsorbed onto the silver nanoparticles, resulting in the ohmic contact at the interface of an electrode and organic semiconductor by lowering the energy barrier for hole injection. The on-current of 8×10^{-9} A and carrier mobility of $2 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{V \cdot s}$ were measured at gate voltage of -60 V. These on-current and mobility values are lower than those reported by another group [9]. This discrepancy might be due to the deficient growth of a crystalline phase in the organic semiconductor layer. It is expected that the electrical performance can be more improved by additional process optimization such as proper heat-treatment condition and use of self-assembled monolayers between the dielectric and organic semiconductor layer [10,11].

CONCLUSIONS

The monodisperse silver nanoparticles with the size of 20 nm were synthesized using polyol method and the metal ink containing synthesized silver nanoparticles was prepared. The metal ink was printed using a piezoelectric DOD ink-jet printing device, followed by heat-treatment at 200°C to fabricate a conductive pattern. The transistor based on the printed silver electrode was fabricated. The on-current of 8×10^{-9} A and carrier mobility of $2 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{V \cdot s}$ were measured.

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