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Inkjet-printed copper electrodes using photonic sintering and their application to organic thin-film transistors

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ABSTRACT

We report on copper (Cu) electrodes fabricated with inkjet-printed nanoparticle inks that are photonic sintered on a polymer dielectric layer and their application to source and drain electrodes in organic thin-film transistor (TFT). By using photonic sintering with a radiant energy density of 9 J/cm^2, printed Cu nanoparticle layers on a glass substrate showed very low electrical resistivity levels of 7 μΩ cm. By optimizing the sintering conditions on polymer dielectric, the pentacene-based TFT using these printed Cu electrodes showed good mobility levels of 0.13 cm^2/Vs and high on/off current ratios of about 10^6. In addition, we revealed that the crystal grain growth of pentacene near the printed Cu electrodes was inhibited by the thermal damage of polymer underlayer due to the high radiant energy density of the intense light.

1. Introduction

In recent years, printing technology has attracted considerable attention in research and development because it can be used to fabricate low-cost and large-area electronic devices, using printing technology, which expected to be used in the manufacturing process for flexible displays devices [1–3], printed sensors [4–6], memory devices [7] and radio frequency identification (RFID) tags [8,9]. Although the development of semiconductor inks is very important to realize a high performance circuit, the conductive inks are also the key material for fabricating fully printed thin-film transistor (TFT). Generally, silver (Ag) pastes or Ag nanoparticle inks is widely used because these materials are can easily obtain high levels of conductivity with low sintering temperatures below 150 °C, which is very important characteristic to use on the plastic substrate. In addition, sintering temperatures for Ag nanoparticle inks have drastically decreased due to the recent developments in reduction in nanoparticle sizes [10,11].

Alternatively, copper (Cu) nanoparticle inks have recently attracted attention as a new class of conductive ink, since the Cu is a low cost metal and has higher resistance to the electromigration compared to Ag [12]. However, Cu nanoparticle inks generally require high sintering temperatures above 300 °C to obtain high conductivities [13,14]. To address this problem, photonic sintering using intense pulsed light with millisecond exposure times and a wide range of wavelengths has been reported as the most useful sintering method for the Cu nanoparticles [15–18]. A Cu nanoparticle layer can be converted to a highly conductive layer due to instantaneous heat generation within the layer accompanied by absorption of the intense pulsed light. Photonic sintering can also selectively heat Cu nanoparticle layers, therefore making it possible to significantly suppress the temperature rise in the underlying substrate material.

Some research groups have reported improvements in layer conductivity or the reduction of sintering temperature for Cu nanoparticles, however they have focused on the application to interconnect technologies on flexible polymer film at low temperatures [15–18]. There have been few reports on the application of the printed Cu electrodes to TFT [13,14]. Furthermore, the use of photonic sintering for Cu nanoparticle inks in TFT fabrication has not been investigated to date. In organic TFT, interface control for the source and drain (S/D) electrodes, such as optimization of the physical contact and energy level to the organic semiconductor layer, is the key to achieving high electrical performance. Therefore, it is very important to investigate the use of printed Cu electrodes in organic TFT, which is fabricated with Cu nanoparticle inks that are photonic sintered.

In this paper, we report on the printed Cu electrodes fabricated by inkjet printing using Cu nanoparticle ink and photonic sintering, and their application to the organic TFTs. By using photonic

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sintering, the printed Cu nanoparticle layers exhibited low electrical resistivities. We have investigated the optimized condition of the photonic sintering for Cu nanoparticles to reduce the thermal damage to the underlying polymer dielectric layer. By controlling the light intensity, large deformations in polymer layer resulting from thermal damage by the sintering process were drastically reduced. An organic TFT using pentacene as the organic semiconductor was fabricated and exhibited good electrical performance.

2. Experimental

We used Cu nanoparticle ink purchased from Ishihara Chemicals Co. (Cu-02) for the printed electrodes, which consisted of Cu nanoparticles with average sizes of 70 nm dispersed in organic solvents with a Cu concentration of approximately 50 wt%. The Cu nanoparticle ink was patterned by using an inkjet printer (DMP-2831, Fujifilm Dimatix). In order to obtain a high conductivity, the patterned Cu nanoparticle layers were sintered using a Xenon (Xe) flash lamp, which had a broad emission spectrum ranging from 350 to 1100 nm. Fig. 1 shows a schematic image of the light irradiation system (ES-UX03, Sugawara Laboratories Inc.). To achieve uniform irradiation of the light with high intensity over large areas, a light source unit was used that consisted of nine Xe lamps and a dome mirror. The light intensity of the irradiation system can be controlled by varying the charging voltage, the duration of light pulse and the distance between the top of sample and the bottom of Xe lamp unit.

Fig. 2 shows the organic TFT structure (bottom-gate and bottom-contact configuration) as fabricated and tested for this report. First, an aluminum (Al) layer was vacuum-deposited onto a glass substrate through a shadow mask with a thickness of 50 nm to form the gate electrode. A benzocyclobutene (BCB) polymer (CYCLOTENE™ 3022-35, Dow Chemical) [19] layer (600 nm thickness) was then spin-coated onto the substrate and annealed at 300 °C for 1 h. The Cu nanoparticle ink was patterned with the inkjet printer to form the S/D electrodes on the underlying polymer dielectric layer. After drying at 50 °C for 5 min, the patterned Cu nanoparticle layer was sintered in air with the Xe flash unit with a radiant energy density of 4.4 J/cm^2 and pulse duration of 0.8 ms (FWHM). Next, the substrate was immersed in a pentafluorobenzenethiol (PFBT) solution (30 mM PFBT dissolved in IPA) for 5 min to treat the surfaces of the S/D electrodes [20]. Finally, a pentacene layer with a thickness of 50 nm was vacuum-deposited onto the S/D electrodes.

The surface morphology of Cu electrodes was observed using a field-emission SEM (FE-SEM) (JSM7600FA, JEOL Ltd.) and an atomic force microscope (AFM) (Nanoscope V, Bruker Instruments). The electrical characteristics for the organic TFT were measured using a semiconductor parameter analyzer (4200-SCS, Keithley Instruments). The work function for the electrodes was estimated using photoelectron spectroscopy in air (AC-3, Riken Keiki).

3. Results and discussion

Fig. 3a shows the resistivity of Cu electrodes as a function of the radiant energy. Here, a single flash light was irradiated to the

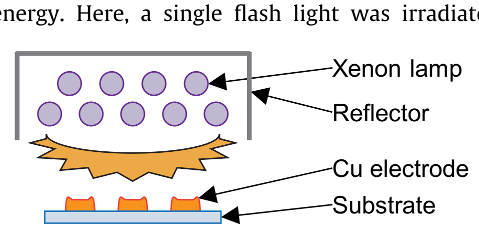

Fig. 1. A schematic diagram of the irradiation system with Xenon (Xe) flash lamps.

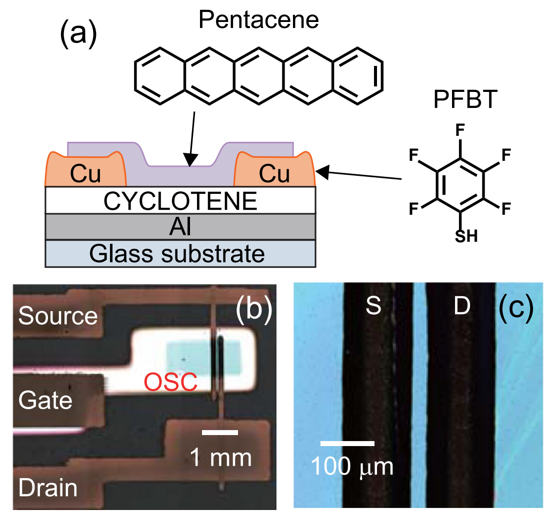

Fig. 2. (a) The device structure of pentacene TFT and the molecular structure for pentacene and PFBT. Microscopic photographs of (b) pentacene TFT and (c) channel region.

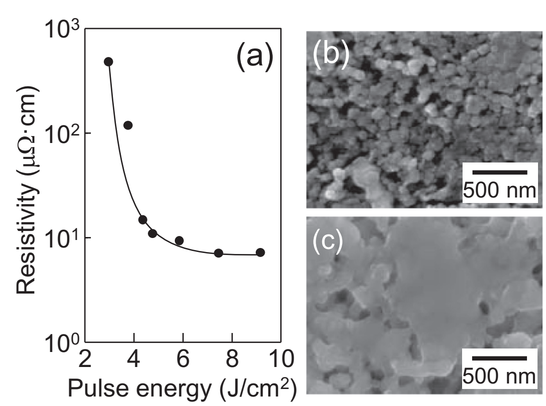

Fig. 3. (a) Relationship between the resistivity of Cu nanoparticle layer and radiant energy density from the flash lamp. (b) SEM image of Cu nanoparticle layer before photonic sintering. (c) SEM image of Cu nanoparticle layer after photonic sintering with 5.9 J/cm^2 energy density.

inkjet-printed Cu nanoparticle layer on glass substrate, such that the variation in light intensity was less than 10% over an area of 4 cm × 4 cm, providing very good uniformity in the radiant energy across the sample substrate (2 cm × 2.5 cm). The resulting thickness of Cu nanoparticle layer was about 300 nm. The resistivities decreased with increases the radiant energy. Low resistivities of less than 10 μΩ cm, which are the same order as the resistivity for bulk Cu, was achieved by irradiating the samples with more than 5 J/cm^2 of radiant energy. The lowest resistivity of 7 μΩ cm was achieved with a light intensity corresponding to an energy density of 9 J/cm^2. Fig. 3b and c show SEM images of the surface of Cu nanoparticle layer before and after flash lamp irradiation with an energy density of 5.9 J/cm^2, which resulted in fused Cu nanoparticles. These results indicate that the Cu nanoparticles were sintered instantaneously by the generated thermal energy resulting from absorption of radiant energy from the high intensity Xe flash lamps.

To employ these inkjet-printed Cu layers to the S/D electrodes in organic TFTs, the sintering conditions for the Cu nanoparticle layer on the polymer dielectric were optimized. The Cu nanoparticle layer was patterned by inkjet printing on a BCB polymer layer with a line width of 200 μm. Fig. 4 shows the cross-sectional