Improvement of mechanical durability on organic TFT with printed electrodes prepared from nanoparticle ink

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Abstract: We investigated a mechanism of improving adhesiveness depending on sintering temperature for printed silver (Ag) electrodes prepared from nanoparticle ink on an insulating polymer layer as the under layer. The adhesion strength significantly improved by sintering the Ag electrodes at a temperature above the glass transition temperature (T_g) of the polymer layer. In the sample with improved adhesiveness, the interfacial fusion between the printed Ag electrodes and polymer layer was observed in a cross sectional scanning electron microscope image. Based on this mechanism, we have successfully demonstrated the improvement in mechanical durability of organic thin-film transistors (TFTs) with printed Ag electrodes. The degradation of the organic TFTs after applying bending stress was significantly suppressed by interfacial fusion.

Keywords: Organic thin-film transistor, Silver nanoparticle ink, Adhesiveness, Bending durability

1. Introduction

Printed electronics have attracted considerable attention because the printing process can be used to fabricate large-area electronic devices on flexible plastic substrates at low cost. These technologies are expected to be used in the manufacturing process for large-area flexible displays^{1,2,3}, photovoltaic cells^{4,5}, and low-cost radio frequency identification tags^{6,7,8}. Although various printable materials, such as metal pastes and conductive polymer inks, have been developed, silver (Ag) nanoparticle ink is one of the most promising candidates for printable electrodes with high conductivity at low sintering temperature. Specifically, the sintering temperature of Ag nanoparticles has decreased due to the reduction in nanoparticle size compared to conventional Ag paste^{9,10}. We recently reported on a high performance organic thin-film transistor (TFT) with printed Ag electrodes prepared from nanoparticle ink at a low temperature (approx. 100°C).¹¹ This report is important in the integration of electronic devices on plastic substrate.

With Ag paste, the adhesiveness is improved by introducing a binder polymer with some adhesive substituent groups for the under layer^{12,13,14}. Since the binder polymer is often crosslinkable, the sintered Ag electrode, while exhibits high resistivity for mechanical stress due to these binder polymer networks. However, Ag nanoparticle ink generally contains less or no binder polymers to reduce resistivity. Therefore, improving adhesion strength with printed Ag electrodes using nanoparticle ink is difficult. Taking into account the mechanical durability of electronic devices after bending stress, the adhesiveness of electrodes is very important. However, there is little information on improving the adhesion strength of printed Ag electrodes prepared from nanoparticle ink on various polymer under layers^{15,16}.

We investigated the adhesion strength between printed electrodes using Ag nanoparticle ink and a polymer insulator, and attempted to improve the adhesiveness by changing the sintering temperature. The adhesiveness of the printed Ag electrodes markedly improved by sintering at a temperature above the glass transition temperature (T_g) of the polymer insulator. In the Ag electrode improved adhesion strength, the interfacial fusion between the Ag electrodes and polymer insulator was observed in a cross sectional image using a scanning electron microscope (SEM). With this mechanism for improving adhesiveness, we attempted to improve the mechanical durability of organic TFT with printed Ag electrodes as the source and drain (S/D) electrode. The degradation in transistor performance after bending stress was significantly suppressed by improving the adhesiveness of the S/D electrodes.

2. Material and methods

Ag nanoparticle dispersed in tetradecane with an Ag concentration of approximately 55 wt% (NPS-JL, Harima Chemicals, Inc.) was used for the printable electrodes. The resistivity and adhesion strength was estimated using a thin Ag film, which was prepared by spin-coating on Teflon and CYTOP. Teflon (AF1600[®], DuPont) dissolved in fluorinert (FC-43, 3M) and CYTOP (CTX-809A, Asahi glass co.) were spin-coated on glass substrates. After spin-coating, the substrates were annealed at 150°C for 1 h. These insulator surfaces were treated with weak oxygen plasma (10 W for 10 s) to improve wettability. The water contact angles after plasma treatment changed from 119 to 101° on Teflon and from 113 to 90° on CYTOP. The Ag nanoparticle ink was spin-coated on the plasma-treated Teflon and CYTOP surfaces. The spin-coated Ag electrodes were sintered at different temperatures from 100 to 180°C. The resistivity

was estimated using the four-point probe system (RGE-12, NPS Inc.). Cross sectional images of the interface were observed by using a field-emission SEM (FE-SEM) (JSM7600FA, JEOL Ltd.). The adhesion strength of the Ag layer was measured by conducting a tensile test. After the spin-coated Ag electrodes on the polymer insulators were sintered, a rod was epoxied vertically on the Ag layer and pulled vertically by using force gauge equipment (FGP-5, Nidec-Shinpo Co.). The adhesion strength was calculated from the tensile strength at the peeling and peeled areas of the Ag layer.

A photograph and a cross sectional image of a bottom-contact pentacene TFT are shown in Fig. 1. PEN film (125 μm , Teonex Q65A, Teijin-DuPont) was used as the substrate for the pentacene organic TFT. After planarizing the PEN film surface by coating an insulating polymer, a 50-nm-thick Al electrode was deposited by thermal evaporation through a shadow mask. Next, Teflon or CYTOP was spin-coated on the substrate and annealed at 150°C for 1 h. The thickness of the dielectric layer was 250 nm. The insulator surface was treated with weak oxygen plasma (10 W for 10 s) to improve wettability of the Ag nanoparticle ink. The S/D electrodes were printed using a dispenser (350PC, Musashi Engineering Inc.) and sintered at 150°C for 1 h. The line width and thickness of the printed Ag electrodes were 200 and 1 μm . The channel length and width were 60 μm and 1 mm. Finally, a 50-nm-thick pentacene layer was deposited by thermal vapor deposition. The organic TFT has no encapsulation after device fabrication.

The electrical characteristics and durability of bending stress were measured at room temperature in dry nitrogen by using a semiconductor parameter analyzer (4200-SCS, Keithley Instruments Inc.). As shown in Fig. 1(b), the bending test was carried out by wrapping the PEN film around the rod with various radii from 11 to 3.5 mm. The

organic TFT was stressed to the tensile strain parallel to the S/D electrodes. The durability of organic TFT with printed Ag electrodes was evaluated by repeating the bending stress with a stress speed of 2 s.

3. Results and discussion

Table 1 lists the resistivity and the adhesion strength of the sintered Ag electrodes, which were prepared from spin-coated Ag nanoparticle ink on Teflon and CYTOP layers. On both insulators, the thickness of the Ag electrodes was 300 nm. Their resistivities were almost similar. The Ag electrodes exhibited a low resistivity of less than 20 $\mu\Omega\cdot\text{cm}$ by sintering at a temperature over 120°C. The lowest resistivity of 4 $\mu\Omega\cdot\text{cm}$ was obtained by sintering at 180°C. In contrast, different results were observed in the adhesion strength of the printed Ag electrodes on the Teflon and CYTOP layers. In the Teflon layer, the adhesion strength improved from 0.05 to 0.3 N/mm² by sintering at 160°C. On the CYTOP layer, the adhesion strength was constantly high (approximately 1 N/mm²) at sintering temperatures exceeding 120°C. The adhesion strength at 100°C was difficult to estimate for both insulators because the Ag electrodes were very fragile due to insufficient sintering temperature.

To investigate the cause of the improvement in adhesiveness and the difference in improving temperature, the interface between the insulator and sintered Ag electrodes was observed using an SEM. Figure 2 shows cross sectional SEM images at the interface. The SEM images with weak adhesiveness [Figs. 2 (a), (b), (c), and (f)] exhibited an interspace between the insulator and Ag layer. On the other hand, interfacial fusion was observed in SEM images with improved adhesiveness [Figs. 2 (d), (e), (g), (h), (i)], which were sintered at a temperature exceeding T_g of Teflon (160°C)

and CYTOP (110°C). Although it is difficult to precisely estimate the thickness of interfacial fusion between the Ag electrode and insulator, from SEM images in fig.2, they were estimated to be approximately 50 nm. Therefore, it is believed that improvement in adhesion strength is attributed to interfacial fusion after sintering at a temperature above T_g of under layer.

Next, we measured the mechanical durability of the organic TFT to investigate the relationship between the adhesiveness of the printed Ag electrodes and transistor characteristics. Figure 3 shows the transistor performance before and after applying mechanical stress with a bending radius of 3.5 mm for the organic TFTs with printed Ag S/D electrodes patterned on (a) Teflon and (b) CYTOP. The gate-source voltage (V_{GS}) was swept from 15 to -30 V with a source-drain voltage (V_{DS}) of -30 V. The printed Ag electrodes on both insulators were sintered at 150°C, which was the upper temperature limit of PEN films for thermal resistivity. At this sintering temperature, the adhesiveness of the Ag electrodes on the Teflon layer was insufficient due to it being below T_g . In contrast, as shown in Table 1, the adhesiveness of the Ag electrodes on the CYTOP layer was improved.

Before bending, the transfer characteristics of both devices were comparable. The field effect mobility estimate from the saturation regime was approximately 0.1 cm²/Vs. The on/off ratio exceeded 10⁶. After bending, the organic TFT fabricated on Teflon exhibited significant performance degradation. The on-current decreased with an increase in bending times. On the other hand, by using CYTOP as the gate insulator, performance degradation due to bending stress was markedly suppressed. Figure 4 shows the change in the normalized on-current for these organic TFTs, which were stressed with bending radii of 11, 6.25, and 3.5 mm. The difference in performance

degradation was very small at a large bending radius. However, at a small bending radius, the degree of performance degradation of the organic TFT on the Teflon layer was more serious and differed substantially from that on the CYTOP layer. On the Teflon layer, the on-current significantly decreased to 20% of the initial current after 100 bending times with bending radius of 3.5 mm. On the CYTOP layer, the decrease percentage was only 35% after 100 bending times with bending radius of 3.5 mm. These results indicate that the adhesiveness of printed electrodes largely affects the bending durability of organic TFTs on flexible substrates.

Figure 5 shows microscope photographs of the printed Ag electrodes before and after bending with a radius of 3.5 mm. The Ag electrodes on the Teflon layer had many cracks. On the other hand, serious damage was not observed in the Ag electrodes on the CYTOP layer. Therefore, it is believed that the decrease in the on-current in organic TFT is caused by the increase in resistance of the printed Ag electrodes. Our experimental results show that the mechanical durability of bending stress in organic TFTs can be improved by using electrodes with strong adhesiveness.

4. Conclusion

In summary, we investigated the adhesion strength of printed Ag electrodes prepared from nanoparticle ink. By sintering at a temperature above T_g of the under layer material, the adhesiveness of the printed Ag electrodes improved due to the interfacial fusion between the printed Ag electrodes and under layer. The decrease in the on-current in the organic TFTs was also significantly suppressed by improving the adhesiveness of the printed Ag electrodes. The adhesion strength of printed electrodes is

important for mechanical durability of flexible and bendable electronic devices on flexible plastic film.

Acknowledgments

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Figure captions

Figure 1. (a) Photograph and (b) cross sectional image of bottom-contact pentacene TFT with the printed Ag electrodes as source and drain. (c) Photographs of durability test for bending stress of the pentacene TFT.

Figure 2. Cross sectional SEM image of the Ag layer on (a) – (e) Teflon and (f) – (g) cytop after sintering with the temperature from 100 to 180 °C.

Figure 3. Transfer characteristics before and after bending stress with bending radius of 3.5 mm for the bottom-contact pentacene TFT with printed Ag electrodes fabricated on (a) teflon and (b) cytop.

Figure 4. Change in the normalized on-current for the pentacene TFT fabricated on (a) teflon and (b) cytop after applying bending stress with a radius of 3.5, 6.25 and 11 mm.

Figure 5. Photographs of the printed Ag S/D electrodes before and after bending stress. (a), (b) and (c) show the Ag electrode on teflon. (d), (e) and (f) show the Ag electrode on cytop.

Tables

Table 1. Resistivity and adhesion strength of the spin-coated Ag layer on teflon or cytop after sintering with various temperature.

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Figure 1

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Sintering temperature (°C)		100	120	140	160	180
Resistivity ($\mu\Omega\bullet\text{cm}$)	Teflon	-	18.5	6.07	4.52	3.93
	Cytop	-	14.2	6.96	4.61	3.96
Adhesion strength (N/mm ²)	Teflon	-	0.05	0.07	0.29	0.31
	Cytop	-	1.07	1.01	1.12	1.01