# Auto-patterned Ag signal line by solution-processed printing on zone-defined surface.

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## Abstract

*Ultra-fine Ag line was automatically patterned to the extent of 10 $\mu m$ in width by slit coating on the $10^4$ $mm^2$ glass, which was pre-patterned as hydrophobic and hydrophilic zone by using hydrophobic material. The resistivity of Ag film was about 4 $\mu\Omega \cdot cm$.*

## 1. Introduction

As the glass size for flat panel display has increased, solution-processed print has been interested in the alternative of deposition/photolithography.[1,2] Among solution-based print technologies, Inkjet print is very promising for electronic devices but it is not available to make the narrower metalline than 80 $\mu m$.[3] In this paper, the repulsion characteristic between hydrophilic Ag dispersed ink and hydrophobic surface was applied to contract the coated Ag ink on glass (Figure 1). Hydrophilic solution was attractive to hydrophilic surface but repulsive to hydrophobic surface. As a result, excessive solution can be confined within hydrophilic zone. The similar phenomenon is commonly observed at the hydrophilic water drop on hydrophobic taro leaf. We investigated the feasibility of this method.

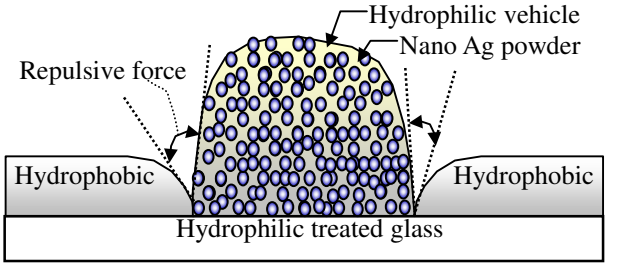


**Figure 1. Confinement of hydrophilic ink on hydrophilic domains surrounded with hydrophobic patterned surface.**

## 2. Experimental

Glass was rinsed with DI (*de-ionized*) water and then cleaned by UV/ ozone generator (wave length; 184 ~ 254 nm, averaged luminous intensity; 15 $mW/cm^2$) to remove contamination and decrease surface energy. UVO-treated glass surface was patterned as hydrophobic and hydrophilic zone with OTS (*octadecyl trichlorosilane* ($CH_3(CH_2)_{17}SiCl_3$)) material by *$\mu$CP (micro-contact printing)* method. OTS solution in anhydrous hexane was coated on the patterned PDMS *(poly-(dimethylsiloxane))* stamp by spin coater (3000 rpm for 30 sec). The stamp was contacted with the substrate for 20 sec. As a result, OTS materials from the raised regions were transferred on the glass. Ag ink was totally coated on pre-patterned glass by slit-coater. Wetted Ag ink layer showed 1 to 5 $\mu m$ thick and gradually confined within hydrophilic surface because of interaction with pre-patterned surface. After Ag ink was defined, the substrate was dried at the room temperature above 30 min to remove the remaining vehicle and then annealed for sintering Ag particles. Ink-jet printing was also performed to confirm the minimum line width on bare glass without hydrophobic surface treatment. Nozzle diameter and drop volume of ink-jet equipment were 40 $\mu m$ and 10 *pl*, respectively. The surface morphology and CD (*critical dimension*) of OTS-patterned surface and Ag line were examined by using SEM (*scanning electron microscopy*) and AFM (*atomic force microscopy*).

## 3. Results and discussion

The diameter of Ag ink droplet jetted from nozzle was about 38 $\mu m$ (Figure 2(a)). Controlled drop distance formed the continuous line. However, the minimum width of the printed Ag line on UVO cleaned glass was as large as 83 $\mu m$ by spreading effect (Figure 2(b)). In order to obtain the narrower

line, we patterned the UVO-treated glass as hydrophilic and hydrophobic zone by using hydrophobic material.

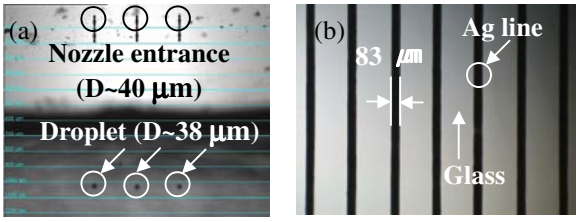


**Figure 2. (a) Ink droplet jetted from nozzle of ink-jet system (b) Ag line printed by Ink-jet on UVO-cleaned surface**

To improve the pattern ability of Ag ink, high hydrophilic glass as well as high hydrophobic zone should be required. When the glass was cleaned by UVO system and then exposed in the atmosphere, the contact angle of DI water drop on glass was less than 10 ° up to 1 hour expose time. This contact angle was calculated as surface tension above 40 *mN/m*, which meant the super hydrophilic surface. OTS material was used to pattern the glass as hydrophobic and hydrophilic zone. OTS material was transferred on glass by contacting OTS-coated PDMS stamp for a moment. Figure 3 showed AFM images of OTS-treated glass and the corresponding photo of DI water drop. When UVO-treated glass was used, the pattern edge was relatively clear (Figure 3(b)). OTS monolayer is formed by Hydrolysis reaction with hydroxyl (-OH) group on glass, so UVO-cleaned glass can make the better pattern shape.[4] Both of them showed the high contact angel 113 °, which value could be convertible into the surface tension of 21 *mN/m* (hydrophobic surface).

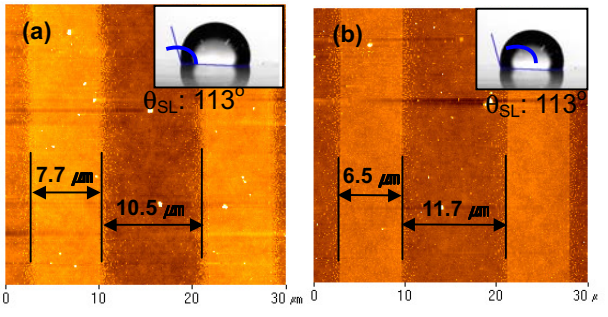


**Figure 3. AFM image and DI water drop photo on OTS-patterned glass by *μCP* at 60 % humidity and 18 °C; (a) bare glass and (b) UVO-treated glass.**

Figure 4 (a) showed the abrupt and uniform OTS pattern, which was 5 *μm* in width and 2 *nm* high. By hydrolysis between OTS and glass, the siloxane bond was formed between OTS and glass (Figure 4(b)).

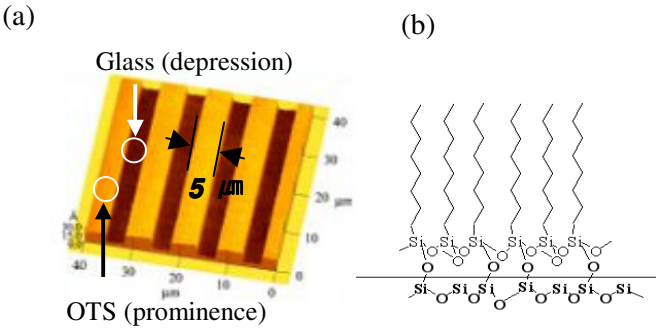


**Figure 4. (a) Surface AFM image of OTS-patterned glass and (b) network structure of OTS-chemisorbed glass.**

Surface tension and viscosity of the dispersed Ag ink were 24.6 *mN/m* and 14.4 *cp*, respectively. The particle size of Ag particle was less than 50 *nm*. Ag ink was totally coated on the OTS-treated glass and then was automatically patterned. Figure 5 showed the photo of overall line pattern with 10, 20, 30, 40 and 80 *μm* width on $10^4$ $mm^2$ glass. Each line was also split by the different line space of 100, 200 and 400 *μm*, respectively. Even though Ag ink was totally coated on pre-patterned glass, the pattern was respectively uniform and clear. Since the hydrophobic OTS material can drastically reduce the surface energy of substrate, hydrophilic Ag ink can be only deposited on the hydrophilic zone. The surface tension is very important to automatically pattern Ag ink.[5] The surface tension of Ag ink have the value between those of OTS-treated zone (21 *mN/m*) and UVO-cleaned glass (40 *mN/m*). In the additive experiments, the ink with the higher surface tension than that of glass was totally wetted but the ink with the lower surface tension than that of OTS-treated surface was totally dewetted.

Figure 6 showed SEM images of metal lines (Figure 5) with 10, 20 and 40 *μm* width. All lines were continuously patterned but the lines below 20 *μm* width were relatively dragged at the line edge part. Ag line with above 40 *μm* width showed 0.25 *μm* thick and dense film with edge sharpness (Figure 6(c)). As the line width was decreased below 20 *μm*, film density was much decreased.

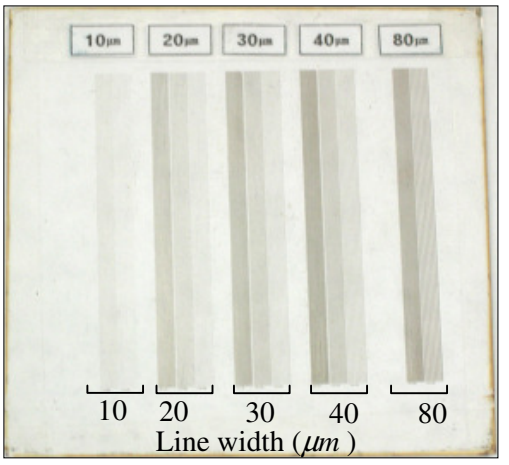


**Figure 5. Photo of the overall line-patterned $10^4$ $mm^2$ glass (line width; 10, 20, 30, 40 and 80 ㎛).**

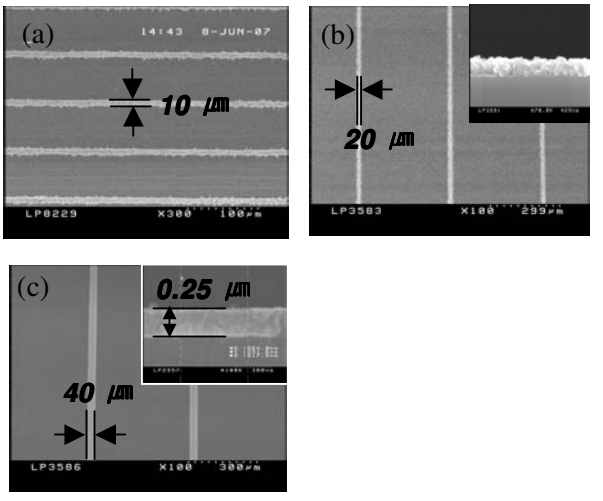


**Figure 6. SEM images of metalline (a) 10 ㎛, (b) 20 ㎛ and (c) 40 ㎛ in width (inset of figure 6(b) and (c) were the cross-section images).**

We fabricated Ag film on glass by slit coater to investigate the dependence of adhesion and resistivity on sintering temperature. Ag film was sintered at 100, 200, 300 and 400 °C, respectively. Figure 7 showed the photo of Ag film after attaching and then detaching 3M Scotch® Cellophane Film 610 to Ag film. Above 200 °C cure, the adhesion on glass was dramatically improved and the peeling ratio was less than 7 %.

The resistivity was also much decreased above 200 °C anneal, compared to 100 °C anneal (Figure 8). The resistivity was about 4 $\mu\Omega \cdot cm$, the film of which was annealed at 200 °C for 30 min at the atmosphere. As the temperature was increased above 200 °C, the resistivity was a little increased. The result might be due to the oxidation of Ag metal.

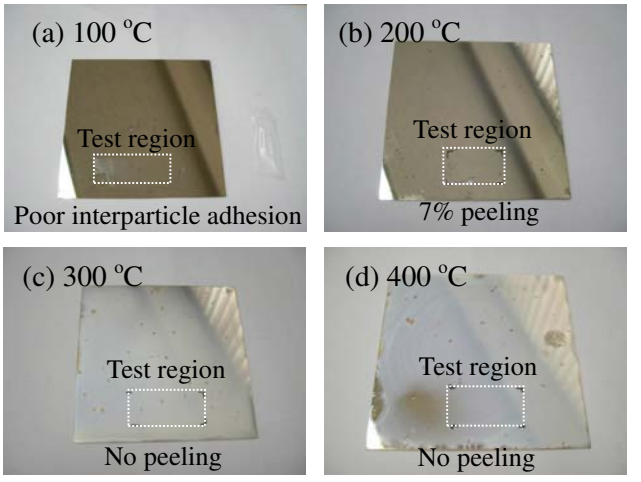


**Figure 7. Photo of Ag films annealed at the various temperature for 30 min (a) 100 °C, (b) 200 °C, (c) 300 °C and (d) 400 °C.**

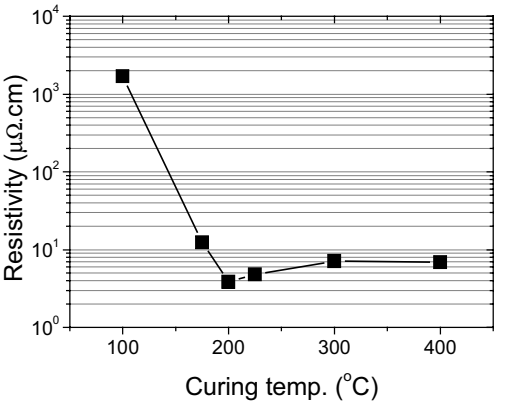


**Figure 8. Resistivity of Ag films annealed at the various temperature for 30 min.**

## 4. Summary

We investigated the feasibility of solution-based fabrication of signal line in order to innovate the cost competition in metallization. In spite of totally coating Ag ink, ultra-fine Ag line was well self-patterned on $10^4$ $mm^2$ glass, which was pre-patterned as hydrophilic and hydrophobic zone. If Ag ink is selectively coated on hydrophilic zone, the excessive

ink can be easily confined within much narrow hydrophilic zone surrounded by hydrophobic zone. A hydrophilic glass was very important to well transfer OTS material on glass and improved the pattern ability. UVO treatment was much effective to increase the surface energy (hydrophilic). Super-hydrophobic zone was patterned on hydrophilic glass by contacting the OTS-coated PDMS stamp. To confine the ink within the hydrophilic domain, Ag ink should have the surface tension between those of hydrophilic glass and hydrophobic surface. Ag line above 40 μm width was very dense and had abrupt pattern edge. The sintered Ag line was to be better conductive (close to the performance of bulk Ag) and adhesive to substrates such as glass.

## 5. References

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