The Effect of Surface Treatment on the Line Formation of Inkjet-Printed Silver Nanoparticles


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ABSTRACT

As line was formed using inkjet printing, how the line width was determined and a degree of bulge occurrence were investigated with changing surface energy of substrate through UV/O3 treatment and a degree of overlap of single droplets. Also, line width experimentally measured was compared with geometrically calculated line width. The number of bulge per unit length was investigated with a degree of overlap. The diameter of deposited single droplet increased as contact angle decreased, and contact angle of deposited single droplet was close to advancing angle. Line width increased as contact angle decreases and a degree of overlap of single droplet increases, and line width was determined by advancing contact angle. Also, the number of bulge per unit length was minimum as a degree of overlap was 50 ~ 60%.

Keywords: Inkjet printing, Surface treatment, Contact angle, Line formation

1 INTRODUCTION

Inkjet printing is considered a promising alternative of micro patterning to conventional photolithography which allows for the drop on demand delivery of various solution based materials such as nanoparticle colloids, polymers, organo-semiconductors and organo-metallics [1-5]. Especially, printing of nano-silver ink has drawn attention which is widely applicable to conductive structures in electronic devices such as displays, logic and memory component including field effect transistor (FETs) and thin film transistors (TFTs) [6-10], radio frequency identification tags (RFID) [11-12].

Conductive patterns in printed electronics require various sizes and morphologies depending on their roles and applications. For example, the gate electrode layer in a bottom-gated transistor must have low roughness [13]. The source and drain need smooth edges, but their width is less critical. For a high-Q inductor or interconnecting wire, conductivity is more important than smoothness or edge uniformity. For organic LEDs, smoothness and film uniformity are important to achieve uniform emission. [3] Nevertheless, reproducing narrowness and uniformity of the width would be among the most necessary conditions for printing conductive lines for electronic applications.

As printing continuous line, many researchers performed the parameters which affect the morphology and width of line. Dan Soltman et al. suggested conditions the stable line is formed with the change of line morphology and width with various substrate temperature, drop spacing, and drop frequency [14]. S. H. Lee et al reported the effect of surface energy and substrate temperature on the change of line width [15].

Generally, the hydrophobic surface induces higher contact angles, leading to smaller droplet spreads. In contrast, larger droplet spreads result from lower contact angles on the hydrophilic surface. In order to fabricate inkjet-printed fine patterns, the surface should be hydrophobic since a hydrophilic surface allows droplets to spread and hence produces larger and broader patterns due to the relatively good wetting of droplets. Also, width, height, and morphology of printed line are changed with degree of overlap of each droplet. As overlap of each droplet is small, continuous line was not formed and shape which a few droplets were merged was observed. As overlap of droplet was large, line has smooth shape [19].

In this study, as line was formed using inkjet printing, line width and a degree of bulge occurrence were investigated with changing surface energy of substrate and drop pitches. As printing single droplet and line, through comparison of measured value from experiment and geometrically calculated value, how line width is determined will be investigated. Also, from number of bulge per unit length with drop pitches, overlap which occurrence of bulge is minimum will be understood.

2 EXPERIMENT

The ink (Harima, NPS-J) contains 64 wt% of spherical silver nanoparticles having average diameter of 5 nm, dispersed in tetradecane. Density and surface tension of the ink and are 1.96 g/ml and 26.6 mN/m respectively. The drop-on-demand (DOD) inkjet printing device (Dimatix, DMP-2831) consists of a cartridge typed jetting head (DMC 11610) having 16 nozzles with a diameter of nozzle of 19 μm and a controller, generating a series of droplets having 9.73±0.17 pl volume, as well as a 2-D traverse stage, monitoring camera, and a working bed. The jetting frequency was fixed at 5 kHz. The ejection velocity of the drops from the nozzle surface was about 4 m/s.
Temperature of laboratory and substrate temperature was 20 °C and 45 °C during the inkjet process.

Contact angle of the ink on the substrate was controlled by applying a hydrophilic treatment on a hydrophobic surface. First, the hydrophobic substrate was prepared by spinning a fluoromopolymer solution, a mixture of Fluorad™ FC 722 and FC 40 (3M) onto the glass (US Corning Pyrex 7740, GER Schott Boro, thickness: 0.7 mm), which was immediately loaded into a convection oven and baked at 110 °C for 10 min. Then in order to increase the hydrophilicity of the surface, UV/O₃ treatment was additionally performed using an UV/O₃ cleaner (AH-1700).

The variation of UV/O₃ treatment time from 0 min to 40 min resulted in the variation of contact angles which were measured by the sessile drop method (DSA 100, Kruss). Line width was measured by Alpha-Step (KLA tensor, ASIQ). After printing 7 lines of 1 cm length, the number of bulge was counted.

3 RESULT

Fig. 1 shows the change of dynamic and static contact angles with UV/O₃ treatment time where \( \theta_a \), \( \theta_r \), and \( \theta_s \) represent advancing, receding, and static contact angle, respectively. The result demonstrates similar behavior of all three contact angles with UV/O₃ treatment time, so that the values of contact angles keep their relative order after treatment. The variation of the contact angles, however, is highly nonlinear with the treatment time. For example, the static contact angle is remained nearly unchanged at about 66° until 13 min of UV/O₃ treatment, but it rapidly decreases to 42° between 13 and 15 min. Then after 15 min, static and receding contact angle was similar. After 25 min, all the three contact angles was almost unchanged.

Diameter of deposited single droplet printed on substrate was determined by volume of jetted single droplet and the equilibrium contact angle. In inkjet printing, Bond number of the used ink which represents ratio of gravitational force and surface tension is much smaller than one. So, the shape of the deposited single droplet can be considered as the part of the sphere. The equation representing relationship between the diameter of deposited single droplet and contact angle is as follows.

\[
D = 2\left(\frac{3V \sin^3 \theta}{\pi(2 - 3 \cos \theta + \cos^3 \theta)}\right)^{1/3}
\]

Here, \( D \), \( V \), and \( \theta \) represents the diameter of deposited single droplet, its volume, and contact angle respectively.

![Fig. 2. Comparison of calculated deposited droplet diameter based on advancing and receding contact angle and measured deposited droplet diameter as a function of static contact angle](image-url)

In Fig. 2, the diameter of deposited single droplet decreases as the contact angle increases. As comparing the diameter of measured single droplet and calculated droplet diameter based on the measured advancing, static, and receding contact angle from Eq. (1), the diameter of deposited single droplet was close to calculated diameter based on measured advancing angle. The diameter of deposited single droplet is determined by angle close to advancing angle. P.C. Duineveld reported that single droplet of liquid with finite receding contact angle has angles close to advancing angle [16].

Like the diameter of deposited single droplet, because Bond number of the ink was much smaller than one, the shape of line can be considered as the part of cylinder. Line

![Fig. 1. Change of Dynamic and static contact angles with varying UV/O₃ treatment time](image-url)
width can be determined by the volume of jetted droplet from nozzle, drop pitch, and contact angle, and equation is as follows.

\[ W = 2 \left( \frac{V \sin^2 \theta}{\rho (\theta - \sin \theta \cos \theta)} \right)^{1/2} \]  

(2)

Here, \( W \) and \( p \) represents the line width and drop pitch respectively.

![Graph showing comparison of measured line width and calculated line width based on advancing contact angle by equation (2) with varying drop pitch.](image)

Fig. 3 Comparison of measured line width and calculated line width based on advancing contact angle by equation (2) with varying drop pitch.

Fig. 3 shows the change of printed line width as varying drop pitch and advancing contact angle, and comparison of the measured line width and the calculated line width based on advancing contact angle. Line width increases as drop pitch and contact angle decrease. Line width was 40 ~ 60 \( \mu \text{m} \) as advancing contact angle is 78.9°, 45 ~ 70 \( \mu \text{m} \) as advancing contact angle 58.6°, 50 ~ 75 \( \mu \text{m} \) as advancing contact angle 48.9°, and 50 ~ 80 \( \mu \text{m} \) as advancing contact angle 33.6°. From Fig. 3, the measured line width agreed with line width calculated by Eq. (2). Droplet falling right ahead of already formed line will flow preferentially into that line [14]. As line is printed with inkjet printer, line width is determined by advancing contact angle.

![Graph showing the number of bulge per unit centimeter with varying advancing contact angle and overlap (\( \theta_a \): advancing contact angle).](image)

Fig. 4 The number of bulge per unit centimeter with varying advancing contact angle and overlap (\( \theta_a \): advancing contact angle)

Fig. 4 shows the change of the number of bulge per unit centimeter as various overlaps of single droplet and contact angles. Overlap was calculated by \((p-D)/D\). The number of bulge was minimum as a degree of overlap of single droplet is 50 ~ 60 %.

4 CONCLUSION

As line was formed using inkjet printing, how the line width was determined and a degree of bulge occurrence were investigated with changing surface energy of substrate through UV/O\(_3\) treatment and a degree of overlap of single droplets. The diameter of deposited single droplet was close to calculated diameter based on measured advancing angle. The diameter of deposited single droplet is determined by angle close to advancing angle. As line is printed with inkjet printer, line width is determined by advancing contact angle. The number of bulge was minimum as a degree of overlap of single droplet is 50 ~ 60 %. Form this result, if dynamic contact angle, volume of single droplet jetted from nozzle, and drop pitch are known, line width can be expected and printing line with minimum bulge occurrence is possible.

REFERENCES