Effects of Inkjet Printing Parameters on Conductive Line Patterns for Flexible Electronics Applications

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ABSTRACT

Aqueous silver nitrate ink (5 moles/liter) mixed with poly(N-vinyl-2-pyrrolidone) (PVP) was employed in a piezoelectric inkjet printing apparatus to construct conductive patterns on ultraviolet/ozone-treated polyimide substrates. At a pulse amplitude of ±38 V, single droplets with a diameter of 36 μm were ejected from the orifice. For array patterns, dots with diameters of about 70 μm were deposited at substrate temperatures of 30 °C and 50 °C. The morphologies of line patterns during the manufacturing process, including those with separated, scalloped, uniform, and bulging features, were adjusted by varying the printing parameters, namely dot spacing and stage velocity. Optimal uniform lines with a width of 44-46 μm were easily obtained at a high evaporation rate of 2.4×10^{-10} g/ms and a substrate temperature of 50 °C. In addition, the conductive silver line patterns have a resistance of 3.4×10^{-5} Ω·cm after being reduced in ethylene glycol vapor at 300 °C for 20 min.

Keywords: silver nitrate, inkjet printing, micro-droplets, piezoelectric print head

1 INTRODUCTION

Light, flexible and recyclable produces are dramatically required, but flexible substrates, such as polyimide, polyethylene terephthalate and metal foils are easy to warpage and form thermal stress during manufacture processes at high temperature. This issue can be resolved by using nano suspensions or precursor inks due to the depressed temperature in the manufacture processes, resulting in increasing reliability of the devices. For ink preparation, inkjet inks must be formulated to fit the physical and rheological properties of fluid dynamic flow during the printed processes.

In our previous study, silver nitrate solutions could be employed into inkjet printing technique [1,2]. However, the precipitation of silver salt around orifice of print head was observed during droplet formation processes, and particularly operated at high substrate temperature of 90 °C. Unless 5 mol/liter (M) solution, it shows stable quality with continuous morphology of the printed patterns on glass substrates and presents a potential development as ink materials.

In order to widen operation conditions having little influence by environment conditions, the commercial conductive inks consist mainly of metallic matters, special contents, and solvents to prepare suitable fluid properties [3,4]. In addition, the geometric control of inkjet printing features can be achieved by adding additives into inks, operating under various printing conditions, and modifying surface properties of various substrates. Lee el at. have successfully printed continuous silver lines in the width range of 48-139 μm which were achieved according to surface conditions controlled by surface energy and substrate temperature below 90 °C [5]. For the application of solar cell, depositing fine lines with a high aspect ratio for silicon cells could open up an opportunity to reduce the grid line separation distance to collect charge careers as efficient as possible [6]. Altough current literatures have sucessfully adopted commercial nano particle inks, the complex ink compositions are hard to realize the actual mechanism and characteristics on controling printing quality.

The present paper summarizes these results along with some additional results obtained for variation of inkjet printing quality. After reduction step of printed line patterns, the surface morphology and resistance of conductive lines are discussed.

2 EXPERIMENTAL METHOD

2.1 Preparation of Silver Nitrate Inks and Polyimide Substrates

Silver nitrate ($AgNO_3$) of 8.5 g and poly(N-vinyl-2-pyrrolidone) (PVP) (molecular weight ~10,000 g/mole) of 0.425 g were directly dissolved in deionized (DI) water of 10 ml to prepare the silver nitrate ink of 5 mol/liter (M). Both compounds were used as precursor and tackifier, respectively. In order to ensure stability of the ink formulation, the viscosity of the prepared inks was measured by a viscometer; Brookfield DV-II+Pro, and the surface tension was measured by a surface tensiometer; FTA 125.

Polyimide (PI) substrates (Kapton, Du Pont Co.) were cleaned by ultrasonic bath of acetone for 30 min followed by a DI water rinse. After drying the cleaned substrates, the UV-O_3 exposure treatment for 30 min was to remove organic contamination on the substrate surface prior to printing process. The high surface energy of hydrophilic substrates was then prepared and subsequently printing procedures were conducted.

2.2 Inkjet Printing

An JetLab®4 was used to deposit the prepared inks and print patterns. This system is equipped with a substrate platen, which can be heated up to 150°C, and can be moved in the X and Y directions with a 5 μm positioning accuracy. A print head with 30 μm nozzle diameter was fixed on a fitting which was mounted on vertical moving axis. Droplets are generated by changing the pulse amplitudes of waveform generator across a piezoelectric actuator and holding it at the optimal conditions for the set pulse times [1,7,8]. The prepared inks were filled into a reservoir in which a negative pressure about 0.29 psi of the reservoir was regulated to prevent ink from leaking from the nozzle of the print head.

During printing process, the gap between print head and substrate on the planar moving stage was adjusted to 0.5 mm, which was equal to the distance of droplet observing setup. Array patterns were printed with a dot spacing of 200 μm. The straight lines were constructed with the dot spacing of 20, 30, 40 and 50 μm at various stage velocity ranged between 1-10 $mm \cdot s^{-1}$. In addition, the critical factor of substrate temperatures was heated to 30 °C and 50 °C.

2.3 Characterisation

The equilibrium contact angle (θ_{eqm}) between the prepared ink and substrates was combined with piezoelectric printing technique about the detail experimental progress described previously [1]. After the desirable patterns were printed on the treated PI substrates, the samples were dried under ambient conditions. Subsequently, the conductive silver patterns were reduced in ethylene glycol vapor at 300 °C for 20 min [3,4,9]. The morphology and feature sizes of patterns were analyzed by OM (optical microscopy, OPTEM), alpha-step profilometer (KLA-Tencor/AS-IQ) and SEM (scanning electron microscope, ZEISS/EVO-50xvp). The resistance was meaured by four-probe method.

3 RESULTS AND DISCUSSION

In previous studies, the disheveled and decentralized patterns were easy to generate using dilute and concentrated silver nitrate inks [1]. In this study, the inkjet printing conditions of silver nitrate/PVP ink were investigated. This ink was a water-based solution containing 5 M silver nitrate in DI water with less amount additive of PVP. All ink contents are totally dissolved into DI water; hence this stable ink shows colorless. The adjusted ink concentration was around 47 wt % with the weight ratio of 20:1 between silver nitrate and PVP. As 4.35 g/cm^3 was taken as the silver nitrate density, 1.16 g/cm^3 as the additive density and 1.0 g/cm^3 as the DI water density. The ink density was about 1.54 g/cm^3. Additionally, the prepared ink had a surface tension near 48.74 $mN \cdot m^{-1}$.

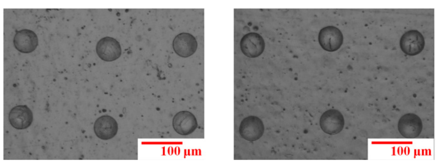
3.1 Dots

According to our previous studies, the silver nitrate inks without PVP addition are easy to form the decentralization of printed patterns on the hydrophilic glass plates [1]. At the same printing conditions, the single droplets with volume of 45 pL deposited on the treated PI substrates. The initial coverage area of dots is about 16.62 mm^2 which expands to 72.38 mm^2 with the irregular shape at substrate temperature of 30 °C and 50 °C. (not shown here) In addition, the concentration of residue liquid layer around the orifice increases gradually and even starts to form a thin layer due to the evaporation of the exposed printing ink during the printing process [1]. It may change the characteristics of the droplet behavior in terms of velocity, volume and misdirection. Andersson el at. adopt the surface coating layer on polymer substrates to improve the printing quality of line patterns due to the PVP additive into this layer [10]. Therefore, the PVP compound is added into 5 M silver nitrate ink as a stabilizer, and is available to eliminate the decentralization phem nomenon using its localized improvement ability during pattern drying.

Micro droplets were continuously ejected at an approxiate bipolar waveform. In this study, the minimum pulse amplitudes was ±31 V, below which piezoelectric print head could not produce any droplet. Within optimal operation pulse amplitudes between ±31 V and ±38 V, single droplet formation was ejected for each pulse cycle. The overall droplet jetted process exhibits a similar ejection evolution progress without satellite or undesirable droplets within this range. At the pulse amplitudes of ±38 V, single spherical droplets with diameter of 36 μm were formed. In addition, sequences of single droplets with average velocity of 3.4 $m \cdot s^{-1}$ can obtain sufficient kinetic and ballistic accuracy to impact precise positions on the substrates. Meanwhile, the same droplet behavior performs at 50 °C. All following printing experiments were then adopting single droplet condition at ± 38 V.

After the droplet impaction at substrate temperature of 30 °C, an equilibrium contact angle between ink and substrate was measured about 40°. It exhibited an initial diameter about 69 μm, which was calculated by the relations between the equilibrium contact angle of the ink with the substrate and droplet volume [11-13]. At the heated substrate temperature of 50 °C, the dot diameter was slightly increased to 70 μm due to the viscous reduce while droplet impaction on the substrate. However, the final diameters of adding PVP dots are reduced to 62 μm and 61 μm in Figure 1 (a) and (b). It demonstrates that the PVP additive is helpful to eliminate the pattern decentralization of pure silver nitrate inks.

Based on Hu's mode of evaporation of a sessile droplet on a substrate below 40°, a quasi-steady-state evaporation process of a droplet with spherical cap on a substrate could be predicted by a very simple approximate evaporation rate expression [14]. During drying progress of printed patterns, the solvent of DI water could evaporate in air gradually except the residue contents of PVP and silver nitrate matters remained in the dry patterns. Assuming the evaporation rate of deposited droplets could only consider as the consuming amount of DI water. The evaporation rate of dot on the PI substrate at 50 °C is approximately three times at 30 °C. Therefore, depleting all amount water in dots at both substrate temperatures of 30 °C and 50 °C requires around 390 ms and 130 ms, respectively. Reviewing the literature, Lim et al. investigated the spreading and evaporation of inkjet printed picoliter droplet on a heated substrate [11]. Their results show that the evaporation time is longer than the impact evolution of droplet until its static situation. Therefore, the evaporation progress of printed dots was possible to form the receding behavior. Particularly, the high evaporation rate at substrate temperature of 50 ^{o}C enhances the diameter variation from 70 µm to 61 µm.



(a) (b)

Figure 1: Array patterns of silver nitrate ink (5 M) printed on UV/O_3-treated PI substrates at (a) 30 °C and (b) 50 °C.

3.2 Lines

According to the literature, the maimum dot spacing (Δx_{max}) of adjacent droplets can be related to the contact angle (θ) of the droplet with the substrate and initial droplet diameter (d_0) before impacting on substrate by the following equations:

$$\Delta x_{\max} = \frac{2\pi d_0}{3\beta_{eqm}{}^2\left(\frac{\theta}{\sin^2\theta} - \frac{\cos\theta}{\sin\theta}\right)} \tag{1}$$

$$\beta_{eqm} = \frac{d_{eqm}}{d_0} = \sqrt[3]{\frac{8}{\tan\frac{\theta}{2}\left(3+\tan^2\frac{\theta}{2}\right)}} \tag{2}$$

where extending ratio (β_{eqm}) is the diameter of the spherical cap on the substrate, d_{eqm}, normalized to d_0. From both equations, the maximum dot spacing at substrate temperatures of 30 °C and 50 °C were about 40 µm. In order to connect all printed droplets, the spacing was decrease to 30 µm.

According to the droplet velocity of 3.4 m/s, the arrival time was required only 150 µs. The sequence droplets overlapped a desirable pattern were configured on various kinds of line morphology, including uniform line and bulging formation. The OM images in Figure 2 show that uniform lines are printed at low stage velocity of 1 mm/s due to longer time interval of 30 ms compared with high stage velocity of 50 mm/s. For short time interval of 0.6 ms, the line with bulging formation. In spite of substrate temperatures at 30 °C and 50 °C, both line morphologies were the same except fine width about 47 µm printed at high substrate tempature with stage velocity of 1 mm/s. Both uniform lines widths were small than dot diameter of array patterns. It indiactes that the deposited droplets reorgnanizes imediately. Moreover, obvious receding behavior at line edge is vertival to printed direction, hence the line width is small than dot dimater of 70 µm.

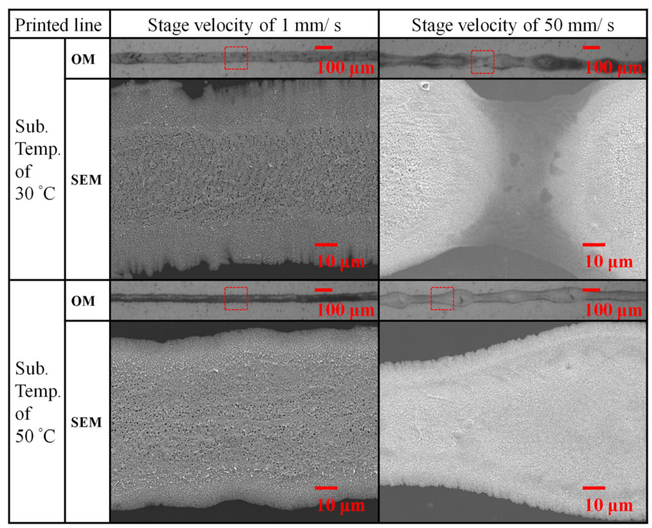


Figure 2: Line patterns printed with various stage velocities and constant dot spacing of 30 µm on UV/O_3-treated PI substrates at 30 °C and 50 °C.

Printing condition		**Reduction condition**		**Printing result**	
Stage velocity, mm/ s	Substrate temp., °C	Temp., °C	Time, min	Resistance, Ω	Resistivity, Ω•cm
1	30	300	20	27.3	3.4×10^{-5}
50	30	300	20	1.7×10^{9}	--
1	50	300	20	58.2	7.3×10^{-5}
50	50	300	20	101.5	9.9×10^{-5}

Table 1: Conductive silver lines printed at constant dot spacing of 30 µm with various stage velocity and substrate tempature.

In Figure 2, the SEM images of printed lines after reduction process at 300 °C for 20 min are magnified at the relative region of red dash rectangle area in the OM images. The reduced silver were uniform distributed into the prtined lines at substrate temperature of 50 °C unlikly the central region with dense silver at 30 °C. However, many voids were distributed on the line surface. Another defect of the dilute distribution was thinned and narrowed between two buldging connection part at stage velocity of 50 mm/s.

3.3 Electronic measurement

Figure 3 shows a schematic illustration of the desined pattern for electronic measurement. The resistivity (ρ) of printed line is measured by four-probe method which can be estimated by the following equation:

$$\rho = R \times A / L \tag{3}$$

where R is the line resistance, A is the cross section area of line, and L is the line length. Table 1 shows that the resistivity of uniform lines at 30 °C and 50 °C are 3.4 x 10^{-5} and 7.3 x 10^{-5} Ω•cm, respectively. At high stage velocity of 50 mm/s, the lines with bulging formation have high resistivity above 9.9 x 10^{-5} Ω•cm at substrate temperature of 50 °C. Furthermore, the line at substrate temperature of 30 °C can't conduct due to the broken line between bulging connection regions.

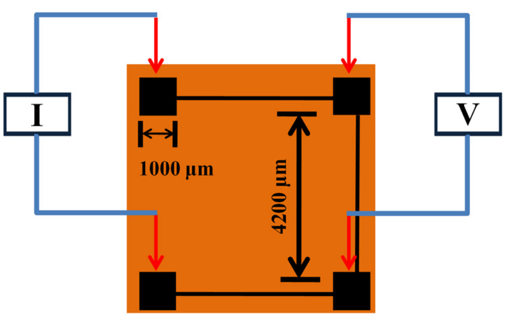


Figure 3: Schematic diagram of four-probe resistivity measurement for silver conductive line.

4 CONCLUSIONS

Printed silver conductive lines of aqueous silver nitrate/PVP ink can be controlled by various dot spacing, stage velocity and substrate tempeature.

1. The similar dot diameter on the UV/O_3 treated PI substrates at 30°C and 50°C was about 60 μm.
2. The resistance of printed lines was inceased with buldging formation.
3. Uniform silver lines of low resistance about 3.4 × 10^{-5} Ω·cm can be printed at dot spcaing of 30 μm with stage velocity of 1 mm/s.

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