Effects of Poly-(N-vinyl-2-pyrrolidone) Additive on Direct-Inkjet-Printed Silver Nitrate Conductive Lines

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ABSTRACT

All-printed electronics has attracted attention due to their fast processing and low cost. Inkjet printing allows circuit components to be directly drawn at a specific area in one step. The printed patterns can be used to fabricate micro-conductors, resistors and capacitors. The formability of printed tracks is thus very important.

This study investigates the inkjet printing of conductive tracks by silver nitrate solution with poly(N-vinyl-2-pyrrolidone) (PVP) additives. Increasing the PVP content improves the formability of printed conductive tracks. However, excessive additive induces a sheet shape precipitation and decreases the conductivity. The optimal line width is 25 μm and the resistivity is about 7.28 μΩ·cm.

Keywords: inkjet, PVP, conductive

INTRODUCTION

One of the most exciting areas in the flat panel display industry is the emergence of flexible displays. In recent years, liquid crystal displays (LCDs) have come to absolutely dominate the displays industry, but LCDs are glass-based solutions. Therefore, many researchers are now working on various approaches to devise displays built on plastic, metal foils, or other substrates [1].

Conventional electronic devices manufacturing processes adopted deposited thin film and lithography techniques to fabricate micropatterns. However, thin film deposition techniques include physical and chemical vapor deposition are not applicable for the polymer substrate due to its high operation temperature (>300° C). In additional, the sputtering process is musch more expensive and materials wasting. For these reasons, the development of convenient, fast processing, and resource saving technique to fabricate conductive lines has attracted more attention in recent years.

In order to solve such processing difficulties, direct writing methods have been considered as an alternate approach [2]. Among direct fabrication methods, inkjet printing has excelled as the most attractive direct patterning technique for versatile designs and fully digital driven with a computer. This study aims to investigate the effect of differences in PVP content on printed conductive tracks.

EXPERIMENTAL

2.1 Inkjet printing condition

Numerous conditions, including driving waveform, backpressure, and ambient conditions can be adjusted in the inkjet printing system. In order to simplify the complex printing process, some conditions were kept constant in this study. Based on Shiled's results, a dwell time of 5 μs was chosen [3-4]. In order to capture high quality images and satisfactory generation of regularity and repeatability of droplets, use 1000 Hz frequency to prevent improper wave propagation and generate sufficient illumination from LED light. An MJ-AT-01 piezoelectric printhead, which is squeeze mode device manufactured by MicroFab Technologies Inc., is employed in this study. The diameter of the printhead nozzle orifice is 30 μm.

A schematic diagram of a typical bipolar pulse waveform employed in this study is shown in Fig. 1. Bipolar voltage signals was used to minimize the certain of unwanted satellite droplet and asymmetric droplet formation, which skew the droplet trajectory and cause droplet misregistration at designated sites [5]. The waveform was set to be 2 μs for t_{rise}, 5 μs for t_{dwell}, 2 μs for $t_{fallrise}$, 5 μs for t_{echo}, and 2 μs for t_{final}. Slow rising time is used to prevent air from being sucked into the tube. The rise and fall voltages were set to equal but opposite potentials. The primary variable of this study is the magnitude of the voltage applied. A slightly negative backpressure about 0.2 kpa was applied at the reservoir to control the liquid level near the orifice. All printing experiments were carried out at room temperature and in ambient atmosphere.

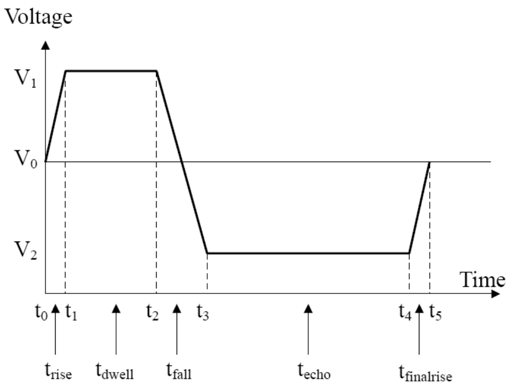


Figure 1. A schematic diagram of a typical bipolar waveform

2.2 Preparation of silver conductive lines on a Kapton substrate

5M silver nitrate solution (Stream Chemicals Inc.) with 1 wt% and 10 wt% poly (N-viny1-2-pyrrolidone) (Tokyo Kasei Kogyo Co., Ltd) as protect agent were chosen to compae with pure 5M silver nitrate solution in inkjet printing conductive tracks. Properties of these fluids are shown in table 1.

A 2 cm x 2 cm Kapton film was cleaned with acetone and deionized water to remove the particles and organic contaminants on the surface. $AgNO_3$/PVP inks with different concentrations were printed by an inkjet printer onto the PET substrates.

Table 1. Properties of the liquids employed in this study

Liquid (unit)	Viscosity (mPa·s)	Surface tension (mN·m^{-1})	Specific gravity (g·cm^{-3})
$AgNO_3$	2.12	49.58	1.518
$AgNO_3$+ 1 wt%PVP	2.33	47.15	1.516
$AgNO_3$+ 10 wt%PVP	2.47	44.95	1.663

2.3 Reduction and chracterization

After printing patterns, the substrate was first dried in an oven at 70˚C for 5 min to remove the solvent. The ethylene glycol vapor reduction approach was employed to fabricate conductive tracks directly from silver nitrate solution by inkjet printing, as shown in Fig. 2. The silver nitrate precursor can be reduced in ethylene glycol vapor at low temperature (150° C) for 30 min [6].

The X-ray diffraction (XRD) experiment was conducted on a Rigaku D/MAX-IIIV X-ray Diffractometer using Ni-filtered Cu-Kα radiation with a scanning rate of 4°min^{-1} at 30 kV and 20 mA. The samples were also observed by optical and scanning electron microscopy (JEOL FE-SEM 7001, Japan) to examine the microstructure as well as measurement of line width and morphology.

Figure 2. Experimental setup of the ethylene glycol vapor reduction

RESULTS AND DISCUSSION

In the piezoelectric inkjet printing processes, the main parameters to control the droplet formation behaviors are liquid properties (including surface tension, viscosity and specific weight) and physical driving force of the printhead (including pulse voltage and shape). Croucher and Hair had proposed a range of surface tension and rheological properties of inks for use with Drop-on-Demand inkjet printing. The ink with viscosity value between 1-10 mPa and surface tension on the order of 35 mNm^{-1}could be employed for inkjet printing processes [7]. In this study, the synthesized $AgNO_3$/PVP inks are satisfied with required properties. (as shown in Table 1.)

The conditions of droplet formation and injection with different $AgNO_3$/PVP inks were shown in Fig. 3. It can be found, the droplet velocity decrease with the increase of PVP content. This is due to the liquid viscosity increased with the added PVP.

The printed arry were shown in Fig. 4. It can be observed the added PVP can improve the formability of printed dot. The average printed dot size is were shown in Table 2. The added PVP content increase the printed dot size. After determines the dot diameter on the substrate, lines were printed on the substrate with a droplet overlap varying from 20 to 60%. The droplet overlap is defined as the ratio of the length of the overlap between two neighboring droplets to the individual droplet diameter on the substrate as shown in Fig. 5.

Fig. 6 shows the optical microscope images of inkjet-printed $AgNO_3$/PVP lines on Kapton substrate at room temperature. The width of lines of each ink slightly increases with increasing the droplet overlap. The higher PVP content can improve the line formability under low drop overlap ratio, the added PVP in $AgNO_3$ solution can restrain the droplet retraction during the impact process. Nevertheless, the increased of PVP content also increase the width of printed tracks.

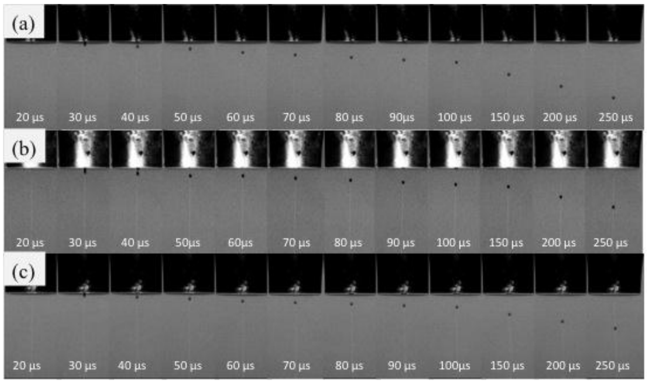


Figure 3. Experimental observation of droplet formation (a) 5 M $AgNO_3$ solution, (b) 5 M $AgNO_3$+ 1 wt% PVP, and (c) 5 M $AgNO_3$+ 10 wt% PVP under the single pulse, T_{rise} = 2, T_{dwell} = 5, T_{fall} = 2, T_{echo} = 5, $T_{finalrise}$ = 2 μs and voltage = 12V driving condition.

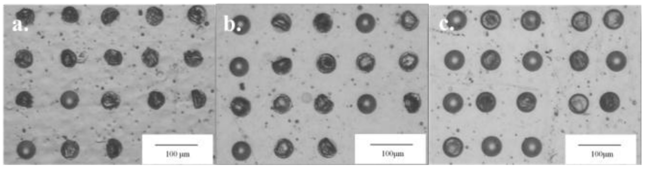
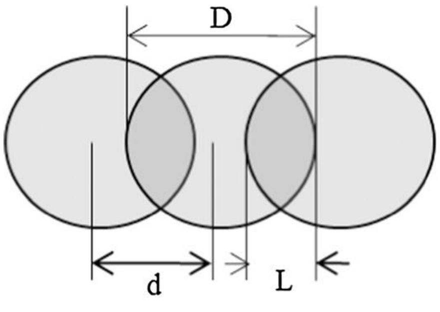


Figure. 4 Printed patterns obtained with (a) silver nitrate solution and silver nitrate solution with (b) 1 wt% and (c) 10 wt% PVP.

Table 2. Printed dot size of the liquids in this study

	Dot size (μm)
AgNO3	40.63 ± 1.92
AgNO3 + 1 wt% PVP	44.66 ± 3.14
AgNO3 + 10 wt% PVP	48.49 ± 2.10

After the reduction treatment, the resistivity of printed $AgNO_3$, $AgNO_3$+1 wt% PVP, and $AgNO_3$+10 wt% PVP were 13.52, 7.28, and 9.33 μΩ·cm, respectively. All printed patterns were confirmed by XRD, and all shows pure silver peaks. Figure 7. shows the SEM images of microstructure of printed patterns. It can be found, after 1 wt% PVP added, the reductive silver exhibit some aggregation particle. The density of reductive silver is slightly higher than pure $AgNO_3$ ink. When the PVP additive increases to 10 wt%, the microstructure present some sheet-shape precipitations. The formation of sheet-shape precipitation causes the degradation of the conductivity of printed conductive tracks due to the discontinuous microstructure. However, the added PVP is effective to increase the adhesion of silver nitrate solution on Kapton substrate. The $AgNO_3$+ 10 wt% PVP solution printed conductive tracks on Kapton can endure over 100,000 times 90° bending test, and still keep its conductivity.



$$\text{Droplet overlap} = \frac{L}{D} \times 100\ \%$$

Figure. 5 Schematic diagram of overlapped neighboring droplets forming a line

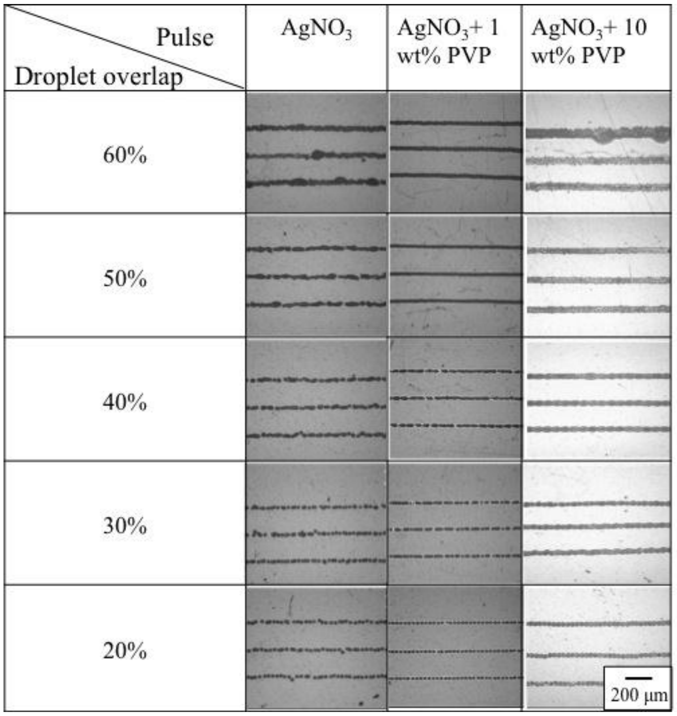


Figure. 6 Optical microscope images of inkjet-printed $AgNO_3$/PVP lines on Kapton substrate at room temperature

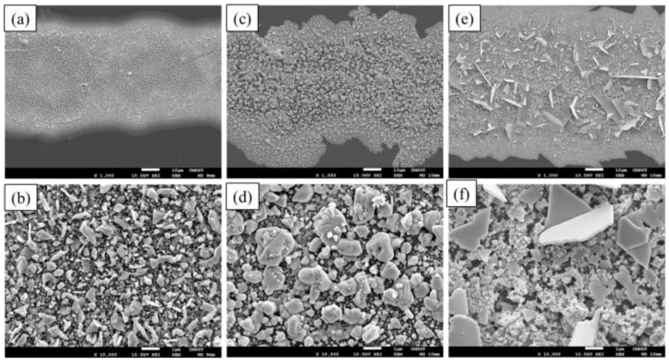


Figure. 7 SEM images of microstructure of printed patterns obtained with (a) silver nitrate solution and silver nitrate solution with (c) 1 wt% and (e) 10 wt% PVP. (b), (d), and (f) show corresponding magnified images.

CONCLUSIONS

In this study, we successfully use $AgNO_3$/PVP solution to directly fabricate conductive patterns by inkjet printing. The printed pattern can be easily reduced in one-step low-temperature (150 ℃, 30 min) thermal process and can achieve resistivity of 7.28 μΩ·cm, which is suitable to be used in printed circuits and interconnect. It is found that the proper content of PVP additive is effective to improve the printed patterns formability, and increase the conductivity of printed circuits. However, the excessive PVP content might cause the decrease of conductivity due to the formation of sheet-shape precipitation.

ACKNOWLEGEMENT

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