Low Temperature (80 ^{0}C) Sinterable Particle Free Silver Ink for Flexible Electronics

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Abstract—**For the emerging field of flexible printed electronics, ink compatibility with substrate is always required. However, most of the commercial silver nanoparticle-based inks are not compatible with flexible substrates, as they need high- sintering temperatures (~150-250 ^{0}C). In addition, silver nanoparticle-based inks have several serious problems such as a complex synthesis protocol, high cost, particle aggregation, nozzle clogging, reduced shelf life, and jetting instability. These shortcomings in conductive inks are barriers for their wide spread use in practical applications. In this work, we demonstrate a silver-organo-complex (SOC) based particle free silver ink which can decompose at 80 ^{0}C and becomes conductive at this low temperature. The inkjet-printed film from this ink exhibits not only high conductivity but also excellent jetting and storage stability. To demonstrate the suitability of this ink for flexible electronics, an inkjet-printed film on flexible polyimide substrate is subjected to bending and crushing tests. The results before and after flexing and crushing are very similar, thus verifying the excellent tolerance against bending and crushing for this ink as compared to the commercial nanoparticles based ink.**

Keywords—silver-organo-complex (SOC) ink, low-temperature sintering, inkjet-printing, flexible, bending and crushing test

I. Introduction

Inkjet printing of metal nanoparticles based inks have widely been used and commercially available for digital pattering in the field of microelectronics. But, in nanoparticles (NPs)-based inks, the metallic dispersion in ink should be stable to aggregation and precipitation for reproducible performance. Therefore, an addition of a stabilizing agent, which is usually a polymeric material, is required. After printing and drying, the resulting pattern is composed of conducting metallic NPs capped with organic stabilizers that act as an insulator. Due to the presence of such organic between the particles, the number of percolation paths is limited, and the conductivity of the printed pattern is too low to be of practical importance. To obtain a conductive pattern, an additional, post-printing treatment is usually required. Generally, sintering temperatures of around 150-250 ^{0}C for 1-2 h is necessary to remove organic moieties from the film [1].

In recent years, development of smart electronic ink such as metal-organo complex (MOC) based inks have shown great potential in the electronic industry for the fabrication of conductive circuits and electrodes [2]. Several ink-formulations are reported based on MOC ink with adjusting the ink-chemistry [3-4]. Each one of these ink-formulation has its own sets of advantages and disadvantages. However, one issue is common in all of them, i.e., all of them are still required high-temperature sintering which is usually not suitable for plastic substrates. The design of complex composition, which could meet various requirements such as in situ reduction, viscosity, stability, uniform surface morphology of film with excellent flexibility, and high conductivity at a lower temperature is crucial.

In this work, we have developed low-temperature sinterable novel type silver-organo-complex (SOC) based ink. The as-formulated ink was monitored up to 5 months which confirmed that ink was robust and highly stable with consistent jetting performance. The as-formulated ink was deposited on Kapton substrate with inkjet-printing. The decomposition of ink at 80 ^{0}C leads to uniform surface morphology with conductivity up to 1.68×10^7 s/m with the number of printed layers. In addition, printed film proves to have perfect tolerance against bending and crushing test as compared to commercial nanoparticles based ink.

II. Materials

A. Ink-formulation and Inkjet-Printing

Particle-free ink is based on a silver acetate complex with ethylamine, ethanolamine, formic acid, water, methanol and 2-hydroxyethyl cellulose (HEC) (Mw ~90,000), wherein ethylamine, ethanolamine and formate species act as in situ complexing solvents and reducing agent. HEC acts as both viscosity modifier and adhesion promoter. The detail of ink-formulation and ink-properties is reported in ref. [5]. The SOC ink was printed with Dimatix DMP-2830 material printer using drop-spacing (DS) of 20 µm.

B. Ink Stability Test

The ink's jetting stability is monitored with time using conventional 10 and 1 picoliter (pL) nozzles. In general, evaporation of the ink in the nozzle leads to clogging of the head as well as a decrease in drop mass over time. However, in our ink-formulation low and high boiling amines not only complex with silver, but they act as a co-solvent to suppress the evaporation rate. Fig. 1a shows a graph of the average drop mass monitored over 5 months for 1 and 10 pL nozzles, which was relatively consistent at just under 1.2 and 7 ng, respectively. We have also tested the effect of delay time interval on the number of working jets, as shown in Fig. 1 (b). It is realized that only one nozzle is working after a 90 min delay possibly due to evaporation of ink in the nozzle. However, after 0.1 second purge, all 16 nozzles again restart and follow the same delay trends. It is further realized that delay test with 1pL nozzle shows much better performance than 10 pL nozzle. The reason is obvious due to less opening of 1 pL nozzle (9µm) thus evaporation is much restricted as compared to 10 pL (21 µm) nozzle.

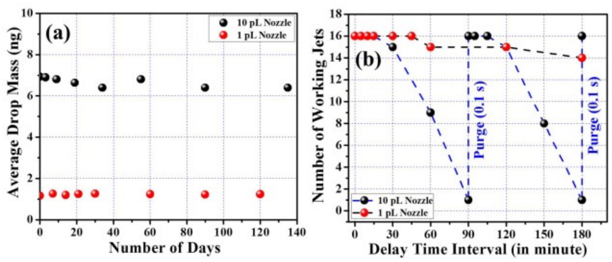

Fig. 1. Ink-jetting stability assessment for 1 and 10 pL cartridges by evaluating (a) average drop mass with the number of days and (b) number of working jets with delay time interval.

III. Conductivity of Printed Film

To evaluate the electrical performance of SOC ink on 50 µm polyimide (PI) substrate, the electrode lines of 40×2 mm were printed as a function of the over-printing layers. Heating was performed at 80 ^{0}C for 5 minutes after printing each layer. After printing 8 layers, films were sintered at 80 ^{0}C for 30 minutes. Similarly, commercial ANP (DGP-40LT) nanoparticles based ink is printed with DS=30 µm to achieve the similar thicknesses of printed films. It should be noted that ANP ink has not shown any conductivity at 80 ^{0}C for 5 min; instead, each layer has to sinter at least for 30 minutes. It can be seen in graph that as-formulated SOC ink shows much better conductivity than commercial nanoparticles ink. Precisely, with 5-8 over-printed layers, we have achieved conductivity of 1.68×10^7 s/m.

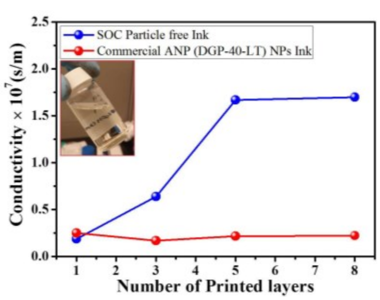

Fig. 2. Measured conductivity as a function of the number of printed silver layers for SOC ink and commercial silver nanoparticles based ink.

A. Bending and Crushing Test

To evaluate the tolerance of printed film against bending, both SOC and commercial inks printed films were bended

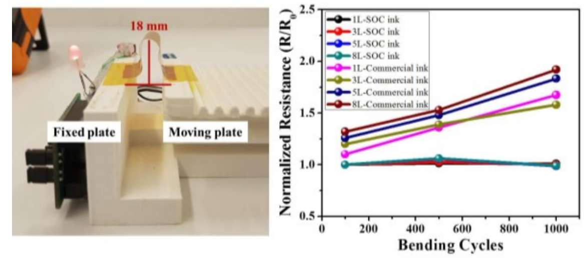

Fig. 3. (a) Bending setup & (b) measured *DC* resistance of printed film with different bending cycles

with radii of 18 mm, as shown in Fig. 3. It is clearly seen in the graph that the printed SOC based silver films exhibit a robust tolerance to bending stresses as compared to commercial ink. In addition, printed films presented no measurable change in resistance while many crushing and folding, shown in Fig. 4.

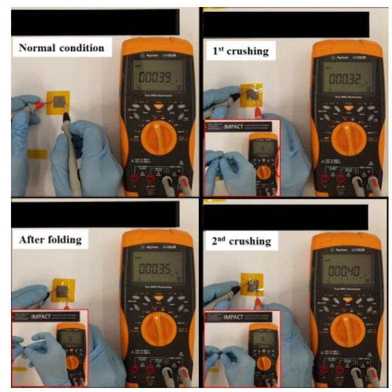

Fig. 4. Folding and crushing test for printed SOC ink based silver film.

IV. Conclusion

In this report, we presented a silver-organo-complex based particle free ink which has excellent jetting stability. In addition, ink exhibited a conductivity of 1.68×10^7 s/m which is much higher than commercial nanoparticles based ink at low temperature of 80 ^{0}C in a shorter sintering time. The bending and crushing test further strength its capability towards flexible electronics working in a harsh condition.

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