Inkjet Printing of Customized Silver Ink for Cellulose Electro Active Paper

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This paper reports a customized silver ink and its inkjet printing process on a cellulose electro-active paper (EAPap). To synthesize a silver ink, silver nanoparticle is synthesized from silver nitrate, polyvinylpyrrolidone and ethylene glycol, followed by adding a viscosifier, hydroxyethyl-cellulose solution, and a surfactant, diethylene glycol. The silver ink is used in an inkjet printer (Fujifilm Dimatix DMP-2800 series) to print silver electrodes on cellulose EAPap. After printing, the electrodes are heat treated at 200ºC. The sintered electrodes show that the thickness of the electrodes linearly increases as the number of printing layers increases. The electrical resistivity of the printed electrodes is 23.5 µΩ-cm. This customized ink can be used in inkjet printer to print complex electrode patterns on cellulose EAPap to fabricate flexible smart actuators, flexible electronics and sensors.

Key Words: Inkjet Printing (잉크젯 인쇄), Silver Ink (은 잉크), Ink Synthesis (잉크 합성), Cellulose (셀룰로오스), Electrical Resistivity (전기저항도)

1. Introduction

Inkjet printing is a very useful low-cost and direct writing technology for micro scale patterning to produce microcircuits,1 metalize of solar cells,2 Fabricate small structures3,4 by ejecting fixed quantity of liquid phase materials onto a substrate. The size of the tiny droplets may vary from 10 to 100 µm diameters. And the liquid phase material refers to a solute dissolved or dispersed in a solvent with some other reagents. The materials are ink jetted from a chamber through a nozzle due to a quick reduction of the chamber volume caused by piezoelectric property.5 For detailed information we refer to reviews covering the subject.6,7 Inkjet printing has some promising advantages over conventional photolithography methods. For instance, it does not need mask for direct patterning8 and, is applicable for large-size substrates.9 It also corresponds to effective use of materials,10 short processing time11 and compact equipment requiring minimal investment.

Since ten years ago, many research efforts have been devoted to develop inkjet printing as a technology to
make micro level conductive patterns, which may substitute screen printing and/or photolithography. This inkjet patterning technique would also be useful for fabricating devices onto temperature-sensitive substrates such as polymer films by solution-based functional materials and also for forming metal interconnects in flat panel displays, to reduce processing cost especially for plasma display and other large size displays. Inkjet printing conditions have been optimized to enable controlled formation of patterned thin films having molecularly flat surfaces. However, in order to obtain enough conductivity for flexible electronics applications, it is necessary to develop a novel conductive ink and control its wetting properties for suitable substrates.

Recently, cellulose has been discovered as a smart material that can be used for flexible sensors, actuators and electronics. From then, many research efforts have been made to utilize the unique properties of cellulose for flexible paper transistor, biosensors, chemical sensors and pH sensors. Re-discovery of cellulose as a smart material, namely electro active paper (EAPap), has been given much attention due to its biocompatibility and eco-friendly behaviors for next industrial applications with interesting functionalities. Inkjet printing of conductive layer on the cellulose EAPap is advantageous comparing with lift-off process and micro contact printing. However, conductive ink for inkjet printing should be customized for the cellulose EAPap.

In this paper, synthesis and customization of a conductive silver ink for the cellulose EAPap are reported, which enable to fabricate several tens of micrometer width electrodes on the cellulose EAPap by inkjet printing. To customize the conductive ink, the ink should be made with silver nanoparticles with narrow size distribution, and their dispersion stability is required for continuous ejecting at inkjet nozzles. Furthermore, highly concentrated silver nanosol is required in order to achieve well-connected fine micro-lined electrode with high conductivity after a heat treatment.

2. Experimental details

Silver nitrate (A.C.S. reagent), polyvinylpyrrolidone, diethylene glycol (99%) and hydroxyethyl-cellulose were purchased from Sigma-Aldrich Korea Ltd. Ethylene glycol (above 99%) and ethanol (above 95 Vol. %) were purchased from Daejung Chemicals and Metals Co. These materials were used without further treatment. Deionized water was used during the whole experimental process.

The synthesis process of conductive silver ink has been already reported. In short, silver nitrate and PVP were dissolved separately in 60 ml of EG by sonication and moderate stirring with heating up to 100°C in an oil bath, respectively. Then silver nitrate solution was injected slowly into PVP solution while stirring vigorously. This solution was then allowed to be gently stirred for 4 hours at 100 ºC temperature. This step results in the formation of PVP capped silver nanoparticles. The resulting solution was washed three times by dispersing in Ethanol and subsequent centrifuging and the final residue of silver nanoparticles with size less than 50 nm was obtained.

After that, a small amount of hydroxyethyl-cellulose (HEC) and diethylene glycol (DEG) were added to the residue of silver nanoparticles. Finally, the conductive silver ink was obtained by sonicating for 1 hour and subsequent ultrasonic homogenizing for 10 minutes.

First, the synthesized silver ink was injected into a printer cartridge. Then the cartridge was kept in refrigerator for at least 2 hours to make sure that there is no air bubble inside the cartridge. Some jetting conditions, for example firing voltage, nozzle number, etc., were changed to the optimal conditions to get better printed patterns.

The cellulose EAPap was prepared through the procedure published elsewhere. Then, the wrinkle free rectangular sized cellulose EAPap was securely attached on the printing base of the inkjet printer. Commercially available cellulose film was purchased from Weifang Co. China. It is a regenerated cellulose film on which surface was treated with glycol. After printing, printed patterns underwent through heat treatment process (sintering) at different temperatures for different time lengths to check the effect of sintering time and temperature on electrical resistivity.

The size of the synthesized silver nanoparticles and the morphology of printed electrodes were measured by scanning electron microscope (FE-SEM, S-4200/ Hitachi) and atomic force microscope (Nanoscope Multimode IVa/Digital Instruments). Commercial inkjet printer
(DMP-2800, Fujifilm Dimatix, USA) was used in this work to print silver electrodes.\(^{17}\) The X-ray diffraction was taken by using an X-ray diffractometer (X’Pert PRO MPD, Philips). The Sonoplus ultrasonic homogenizer and a sonicator (Power Sonic 420) were used to homogenize and sonicate the solution. The resistivity was measured by 4-point probe desk (250 System, MS-Tech., Korea).

3. Results and discussion

The face centered cubic structure of silver particle was confirmed by X-ray diffraction (XRD) graph. In Fig. 1, the XRD pattern of PVP capped silver nanoparticles displays four characteristic peaks at 38.1°, 45.3°, 65.8° and 77.3°, which peaks can be indexed to (111), (200), (220) and (311) crystallographic plans, respectively.\(^{20}\) No diffraction peak of Ag\(_2\)O was detected in this analysis, which means that silver was not oxidized due to capping agent PVP.

The size of the silver nanoparticles was observed by analyzing micro photographs of SEM and AFM images. The SEM image of silver nanoparticles synthesized from PVP having MW 10,000 and reaction temperature 100 °C is shown in Fig. 2. The average size of silver nanoparticles is around 50 nm.

Silver electrode lines were printed on both laboratory made cellulose EAPap and the commercial cellulose film. It is important to mention that the printed electrode lines were continuous without any break. Evenness of the electrode line strongly depends on the surface roughness, amount of wrinkles and surface treatment of the cellulose EAPap.\(^{21}\) Fig. 3 shows micro photographs of as printed but dried silver electrodes on the laboratory prepared cellulose EAPap (a) and the commercial cellulose film (b), and the SEM image of sintered electrode line on laboratory prepared cellulose EAPap (c). The clearness of electrode lines on the laboratory prepared cellulose EAPap and the commercial cellulose film are comparable. The printed electrodes showed much higher line-clearness before heat treatment. After sintering, the lines became little uneven in terms of their width throughout the length.

The effect of number of printing on printed electrodes was also examined. After printing once, the printed pattern was dried with hand drier and another printing was made on the exactly same position. By doing this, single layered, double layered, triple layered and quadruple layered electrodes were prepared. All electrodes were characterized carefully. Fig. 4 illustrates
the SEM images of single, double and triple layered electrodes indicating the comparative thicknesses. The average thicknesses of single, double and triple layered electrodes are 0.25 µm, 0.6 µm and 0.95 µm, respectively.

The thickness distribution along cross-section of printed electrode was analyzed by Alpha-Step Surface Profiler with 0.1% step height repeatability. Fig. 5 shows the thickness profiles across the cross-section of four different samples, such as, single layered, double layered, triple layered and quadruple layered electrodes. Though the thickness distribution of single layered electrode is quite uniform compared to other samples but its thickness at center line is lower than thicknesses at both edges. Higher number of printing causes clear fluctuations in thickness profiles indicating non-uniformity. Importantly quadruple layered electrode has wider line width than other samples. In Fig. 6, the box chart describes mean, median and interquartile range of thicknesses for all the samples in detail. It also indicates that the average thickness increases with the number of printing increases. The bulk resistance across printed electrodes was measured by means of digital multi-meter. Width and thickness of single layer printed electrodes were measured from SEM images. Finally, the bulk resistivity of printed electrodes was calculated. When necessary it was checked with electrical resistivity measured directly using a 4-point probe.

The resistivity varies with sintering temperature and sintering time. From Fig. 7, with higher sintering temperature, resistivity decreases. The longer sintering process also reduces resistivity of printed electrodes. After sintering for 20 min resistivity drastically reduced. Another dramatic decrease of resistivity was observed after increasing the sintering temperature; when sintering
temperature rose from 180 °C to 200 °C, the resistivity decreased from 630 µΩ-cm to 104 µΩ-cm with 10 min sintering. When the sintering time increased from 15 min to 20 min, the resistivity plummeted from 615 µΩ-cm to 183 µΩ-cm at 180 °C sintering temperature. More importantly, regardless of sintering time the resistivity after heating at 230 °C reaches a convergent value around 20~30 µΩ-cm. Though the minimal resistivity, 21.6 µΩ-cm was achieved from 25 min long sintering at 230 °C. But the substrate cellulose is one kind of polymer which is better lower heat treatment. When consider cellulose property, optimal conditions are 20 min and 200 °C. With this optimal condition, the resulting resistivity was 23.5 µΩ-cm, only 9% higher than the minimum resistivity.

4. Conclusions

To summarize, a previously synthesized conductive silver ink was used to print silver micro-lined electrode by using inkjet printing technology. In this work, cellulose EAPap was used as a substrate. It was found that the printed electrodes were continuous without any break and showed electrical resistivity as low as 21.6 µΩ-cm. As the double and triple layered electrodes showed twice and thrice of thickness of single layered electrode, it can be concluded that the thickness and number of printing are linearly related. As the sintering temperature and time increase, the electrical resistivity of silver electrodes decreases. The optimal sintering condition is found to be 200 °C with 20 min, resulting in electrical resistivity of 23.5 µΩ-cm. Further research can be carried out to utilize cellulose EAPap with this printing technology. Cellulose EAPap has many potential applications. Inter-digital transducer (IDT) pattern is one of complicated electrode which enables to various and extensive application of EAPap. Some principal concepts and applications of EAPap with IDT pattern are paper transistors, surface acoustic wave devices, biosensors and gas sensors and, chemical sensors.

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