한국정밀공학회지 제 31 권 8 호 pp. 737-742
J. Korean Soc. Precis. Eng., Vol. 31, No. 8, pp. 737-742
ISSN 1225-9071(Print), ISSN 2287-8769(Online)

http://dx.doi.org/10.7736/KSPE.2014.31.8.737

셀룰로오스 EAPap 용 은잉크 제조 및 잉크젯 프린팅

Inkjet Printing of Customized Silver Ink for Cellulose Electro Active Paper

문성철 [1], Mohammad Abu Hasan Khondoker[1], Abdullahil Kafy[1], Md Mohiuddin[1], 김재환 [1,✉]
Seongcheol Mun[1], Mohammad Abu Hasan Khondoker[1], Abdullahil Kafy[1], Md Mohiuddin[1], and Jaehwan Kim[1,✉]

1 인하대학교 기계공학과 (Center for EAPap Actuator, Department of Mechanical Engineering, Inha University)
✉ Corresponding author: jaehwan@inha.ac.kr, Tel: +82-32-860-7326

Manuscript received: 2014.3.28 / Revised: 2014.6.10 / Accepted: 2014.6.20

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 200℃. 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 structures[3,4] 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 patterning[8] and, is applicable for large-size substrates.[9] It also corresponds to effective use of materials,[10] short processing time[11] 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.[7] This inkjet patterning technique would also be useful for fabricating devices onto temperature-sensitive substrates such as polymer films by solution-based functional materials[12] and also for forming metal interconnects in flat panel displays, to reduce processing cost especially for plasma display and other large size displays.[8] Inkjet printing conditions have been optimized to enable controlled formation of patterned thin films having molecularly flat surfaces.[13] 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.[14] 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.[15-17] 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.[7]

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.[18] 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 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.[19] 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_2O 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,

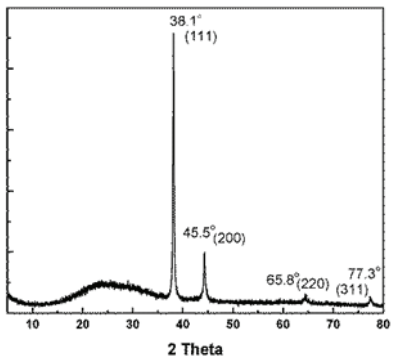

Fig. 1 XRD pattern of Ag nanoparticles synthesized from PVP with molecular weight of 10,000 and reaction temperature at 100 °C

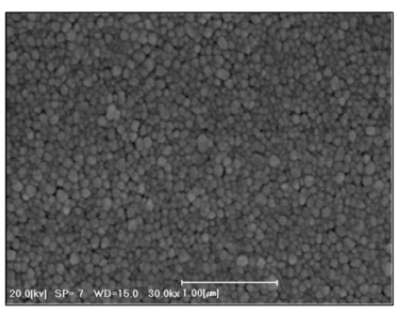

Fig. 2 SEM image of Ag nanoparticles synthesized from reaction temperature at 100 °C and PVP with molecular weight of 10,000

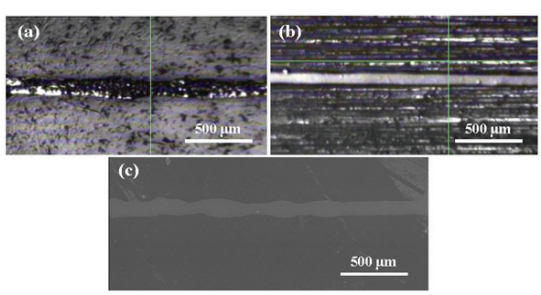

Fig. 3 Photographs of as printed electrodes on (a) laboratory prepared cellulose EAPap and (b) commercial cellulose film. (c) SEM images sintered electrode on laboratory prepared cellulose EAPap

single layered, double layered, triple layered and quadruple layered electrodes were prepared. All electrodes were characterized carefully. Fig. 4 illustrates

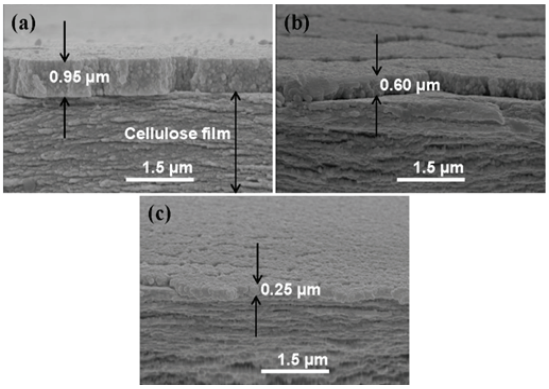

Fig. 4 SEM images of cross-sections of sintered electrodes with (a) triple layer, (b) double layer and (c) single layer

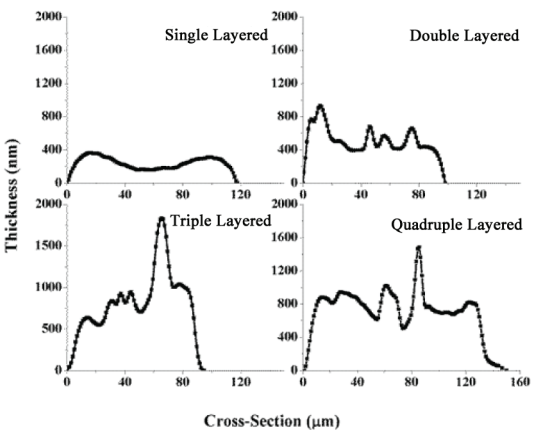

Fig. 5 Thickness profiles across cross-section of printed electrodes for different layers

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

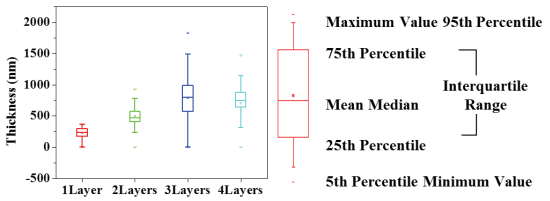

Fig. 6 Comparison between thicknesses of electrodes having different number of layers

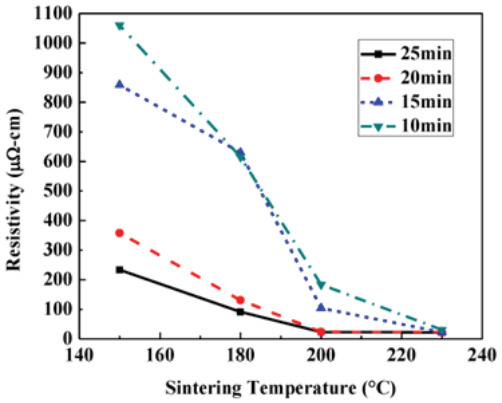

Fig. 7 Electrical resistivity (μΩ-cm) of printed electrodes vs. sintering temperature (ºC) and sintering time (min)

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 ºC 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.

ACKNOWLEDGEMENT

This research was supported by National Research Foundation (NRF-2012R1A2A1A01002087), Republic of Korea.

REFERENCES

1. Sirringhaus, H., Kawase, T., and Friend, R., “High-Resolution Ink-Jet Printing of All-Polymer Transistor Circuits,” MRS Bulletin, Vol. 26, No. 7, pp. 539-543, 2001.
2. Teng, K. and Vest, R.W., “Liquid Ink Jet Printing with Mod Inks for Hybrid Microcircuits,” Proc. of the IEEE Transactions on Components, Hybrids, and Manufacturing Technology, Vol. 10, No. 4, pp. 545-549, 1987.
3. Zhao, X., Evans, J. R. G., Edirisinghe, M. J., and Song, J. H., “Direct Ink-Jet Printing of Vertical Walls,” Journal of the American Ceramic Society, Vol. 85, No. 8, pp. 2113-2115, 2002.
4. Noguera, R., Lejeune, M., and Chartier, T., “3D Fine Scale Ceramic Components Formed by Ink-Jet Prototyping Process,” Journal of the European Ceramic Society, Vol. 25, No. 12, pp. 2055-2059, 2005.
5. Singh, M., Haverinen, H. M., Dhagat, P., and Jabbour, G. E., “Inkjet Printing-Process and Its Applications,” Advanced Materials, Vol. 22, No. 6, pp. 673-685, 2010.
6. Le, H. P., “Progress and Trends in Ink-Jet Printing technology,” Journal of Imaging Science and Technology, Vol. 42, No. 1, pp. 49-62, 1998.
7. Ryu, B.-H., Choi, Y., Park, H.-S., Byun, J.-H., Kong, K., et al., “Synthesis of Highly Concentrated Silver Nanosol and Its Application to Inkjet Printing,” Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 270, pp. 345-351, 2005.
8. Furusawa, M., Hashimoto, T., Ishida, M., Shimoda, T., Hasei, H., et al., “Inkjet-Printed Bus and Address Electrodes for Plasma Display,” SID Symposium Digest of Technical Papers, Vol. 33, No. 1, pp. 753-755, 2002.
9. Shimoda, T., Kanbe, S., Kobayashi, H., Seki, S., Kiguchi, H., et al., “Multicolor Pixel Patterning of Light-Emitting Polymers by Ink-Jet Printing,” SID Symposium Digest of Technical Papers, Vol. 30, No. 1, pp. 376-379, 2002.
10. Miyashita, S., Imamura, Y., Takeshita, H., Atobe, M., Yokoyama, O., et al., “Full Color Displays Fabricated by Ink-Jet Printing,” Proc. of the Asia Display Research Conference, pp. 1399-1402, 2001.

11. Grove, M., Hayes, D., Cox, R., Wallace, D., Caruso, J., et al., “Color Flat Panel Manufacturing using Ink Jet Technology,” Proc. of the Display Works, Vol. 99, 1999.
12. Huang, D., Liao, F., Molesa, S., Redinger, D., and Subramanian, V., “Plastic-Compatible Low Resistance Printable Gold Nanoparticle Conductors for Flexible Electronics,” Journal of the Electrochemical Society, Vol. 150, No. 7, pp. G412-G417, 2003.
13. Minemawari, H., Yamada, T., Matsui, H., Tsutsumi, J., Haas, S., et al., “Inkjet Printing of Single-Crystal Films,” Nature, Vol. 475, No. 7356, pp. 364-367, 2011.
14. Kim, J., Yun, S., and Ounaies, Z., “Discovery of Cellulose as a Smart Material,” Macromolecules, Vol. 39, No. 12, pp. 4202-4206, 2006.
15. Yun, S., Jang, S.-D., Yun, G.-Y., Kim, J.-H., and Kim, J., “Paper Transistor Made with Covalently Bonded Multiwalled Carbon Nanotube and Cellulose,” Applied Physics Letters, Vol. 95, No. 10, Paper No. 104102, 2009.
16. Yun, S. and Kim, J., “Multi-Walled Carbon Nanotubes-Cellulose Paper for a Chemical Vapor Sensor,” Sensors and Actuators B: Chemical, Vol. 150, No. 1, pp. 308-313, 2010.
17. Mun, S., Yun, S., Jung, H., and Kim, J., “Sintering Condition Effect on the Characteristics of Ink-Jet Printed Silver Pattern on Flexible Cellulose Paper,” Current Applied Physics, Vol. 12, pp. e10-e13, 2012.
18. Khondoker, M. A. H., Mun, S. C., and Kim, J., “Synthesis and Characterization of Conductive Silver Ink for Electrode Printing on Cellulose Film,” Applied Physics A, Vol. 112, No. 2, pp. 411-418, 2013.
19. Yun, S., Chen, Y., Nayak, J. N., and Kim, J., “Effect of Solvent Mixture on Properties and Performance of Electro-Active Paper Made with Regenerated Cellulose,” Sensors and Actuators B: Chemical, Vol. 129, No. 2, pp. 652-658, 2008.
20. Chou, K.-S. and Lai, Y.-S., “Effect of Polyvinyl Pyrrolidone Molecular Weights on the Formation of Nanosized Silver Colloids,” Materials Chemistry and Physics, Vol. 83, No. 1, pp. 82-88, 2004.
21. De Gans, B. J., Duineveld, P. C., and Schubert, U. S., “Inkjet Printing of Polymers: State of the Art and Future Developments,” Advanced Materials, Vol. 16, No. 3, pp. 203-213, 2004.