Self-patterned Metal Electrodes by the Fusion Control of Silver Nanoclusters for Inkjet Printing Process

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Abstract

The opportunity of inkjet printing for the fabrication of metal electrodes in electronics applications has been explored for years but the direct fabrication of fine metal electrodes in the scale of tens of micrometers and less has suffered from its limited resolution and reliability. Moreover, the imperfect wetting control of silver ink has caused the short circuit formation between adjacent electrodes, even with a surface energy patterning technique. In this study, a novel self-patterning technique is introduced, which has the capability to convert metallo-organic silver ink to either conductive or non-conductive patterns, as intended. It is found that polyaniline allows the infiltration of metallo-organic silver ink into the voids among polyaniline granules and inhibits the formation of networked silver nanoclusters after a thermal process. With the fusing control layer of polyaniline, conductive and non-conductive patterns were successfully self-differentiated, no matter where metallo-organic silver ink lied down, and the line resistance of the self-patterned metal electrode as fine as 96 µm in line width and 27 µm in line space was as low as 27.55±0.62 Ω/cm.

Introduction

Printed electronics has drawn the attention of researchers due to its inherent nature such as process flexibility and low cost manufacturability for years. The fabrication of various kinds of electronic components such as radiofrequency antennas [1], RC filters [2] and thin film transistors (TFT) [3] has been successfully demonstrated with inkjet printing. Because of the pressure to miniaturize electronic components, the fabrication of electrodes as small as tens of micrometers was an issue and researchers focused on the precise deposition and alignment of ink, as shown in Fig. 1(a). However, direct inkjet printing has a great difficulty in providing such precise deposition and alignment and hence the combinatorial process of inkjet printing and surface energy patterning technique has been intensively explored [4, 5], as shown in Fig. 1(b), where ink is repelled by the low surface energy patterned regions and remains in the high surface energy patterned regions. Although this combinatorial process greatly improves resolution and reliability, it needs an additional process such as photolithography to define surface energy patterned regions. In addition, the surface energy patterning technique has no capability to perfectly control ink spreading so that short circuits are often formed when conducting ink crosses over the low surface energy patterned regions.

Therefore, a new approach has been demanded, which requires less effort of precise deposition and alignment. In addition, it is desirable to actively prevent the short circuit formation when conducting ink is misplaced between electrodes, as shown in Fig. 1(c), where functionally sound electrodes are formed even though metallo-organic silver ink is not precisely deposited.

In this study, the principal mechanism of the self-patterning technique and its opportunity for the fabrication of fine metal electrodes are investigated. In Section 2, experimental details will be described and morphological traits of the self-patterned electrodes will be shown in Section 3. Finally, conclusions will be drawn in Section 4.

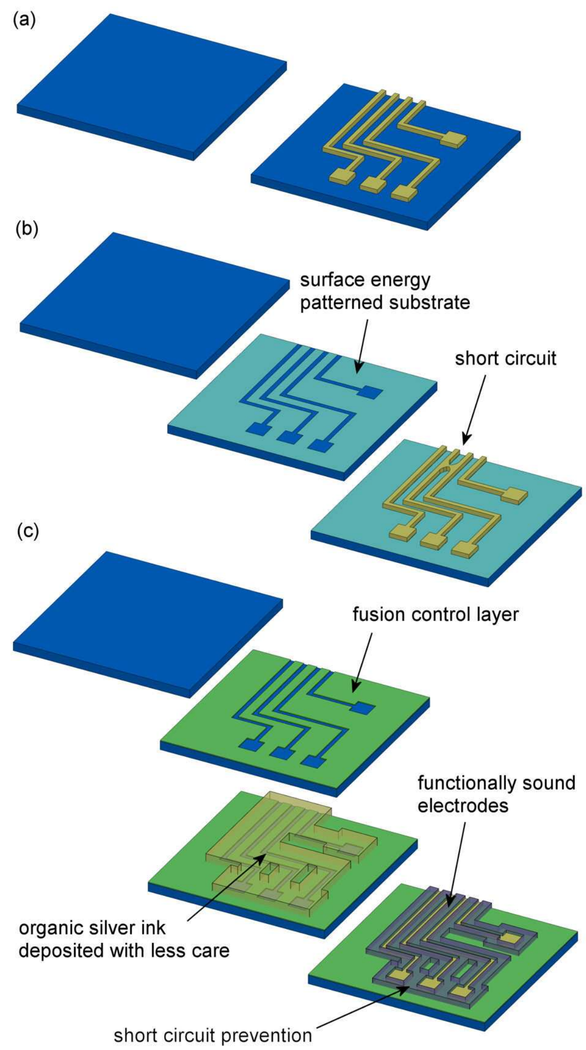

***Figure 1**. Inkjet printing processes, (a) direct inkjet printing, (b) with a surface energy patterning technique, and (c) with the proposed self-patterning technique.*

Experimental Details

Polyaniline (Panipol X, Panipol Ltd, Finland), as a fusion control material, was applied on glass microscope slides (Ref. 10 004 12, Paul Marienfeld, GmbH & Co. KG, Germany) with a spin coater (Spin 300A, Midas System Co., Ltd, South Korea) at 1500 rpm for 30 sec. After soft-baking on a hot plate (GLHP-D3040, GlobalLab, South Korea), the fusion control layer was selectively removed with a laser marker (U-5G, RMI Korea Co., South Korea). The driving current, marking step size and frequency of the laser marker were set at 34.0 A, 5 µm, and 20 kHz, respectively.

As an adhesion promoter, (3-aminopropyl) trimethoxysilane (CAS 13822-56-5, Sigma-Aldrich Co., Missouri, USA) was added to the metallo-organic silver solution (C2080402D5, Gwent Electronic Materials Ltd., UK) at the concentration of approximately 1.78 wt%. After the metallo-organic silver solution was spin-coated at 1500 rpm for 30 sec on the laser-patterned sample, it was dried on a hot plate at 180 ˚C for 5 min. To avoid unwanted pin hole defects, this procedure was repeated once more.

The hard-baking of the sample at 230 ˚C for 20 min converted metallo-organic silver to a metallic state of silver nanoclusters. The electrical and morphological characteristics of silver nanoclusters were measured with a four-point probe (Universal Probe, Jandel Engineering, Ltd, UK) and a source-meter (Model 2400, Keithley Instruments Inc., USA), and a field emission scanning microscope (Nova NanoSEM 230, FEI Company, Oregon, USA), respectively.

Results and Discussion

Figure 2 shows the laser patterned polyaniline sample and the hard-baked polyaniline sample after the deposition of the metallo-organic silver solution.

As shown in Fig. 3, the dried fusion control layer is composed of polyaniline granules, the average size of which is less than 50 nm. Polyaniline has three different oxidation states, pernigraniline (dark gray or black), emeraldine (green) and leucoemeraldine (transparent) [6, 7] and only the emeraldine form of polyaniline is conductive. In this study, the emeraldine form of polyaniline was used as a fusion control material.

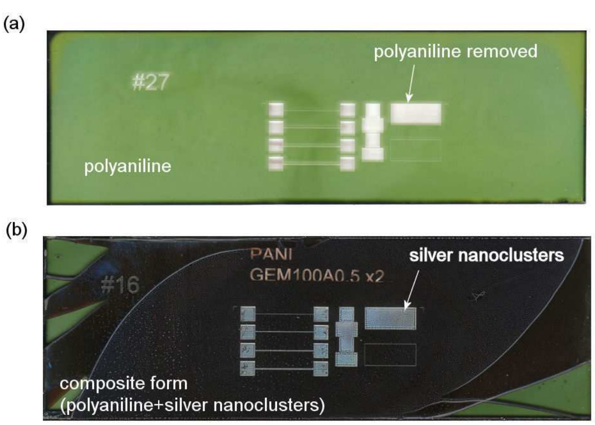

Figure 2. *Self-patterned sample, (a) before and (a) after the deposition of metallo-organic silver.*

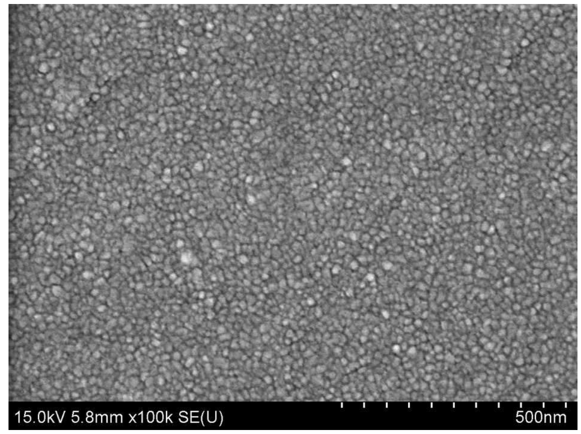

Figure 3. *Morphology of the fusion control layer, composed of dried polyaniline granules.*

Figure 4. *Illustration of the self-patterning mechanism.*

The positive charge of polyaniline in the emeraldine form is stabilized with such molecules as dodecyl benzene sulfonic acid (DBSA). When the metallo-organic silver solution is laid down and permeates into the voids among polyaniline granules, as shown in Fig. 4, the oxidation state of polyaniline is changed due to the negatively charged carboxyl group of metallo-organic silver. As a result, the emeraldine form of polyaniline becomes the non-conductive pernigraniline form and its color changes from green to black, as shown in Fig. 2(b).

Figure 5 shows the morphology of silver nanoclusters converted from metallo-organic silver. Silver nanoclusters are found fused well with each other when there is no fusion control material present. The measured sheet resistance is around 1.70±0.09 Ω/□. On the other hand, if there is the fusion control material present, then silver nanoclusters are hindered from being fused with each other and hence they remain isolated, as shown in Fig. 6. The measured sheet resistance is around 11.2±6.7 GΩ/□ and this composite, polyaniline and isolated silver nanoclusters, could be considered as an insulator.

The insulation characteristic of the composite was measured with two adjacent electrical pads. When these pads are apart at the distances of 10.1, 27.2 and 50.1 µm, respectively, the measured electrical resistance values were 0.03, 519.8 and 1090 MΩ.

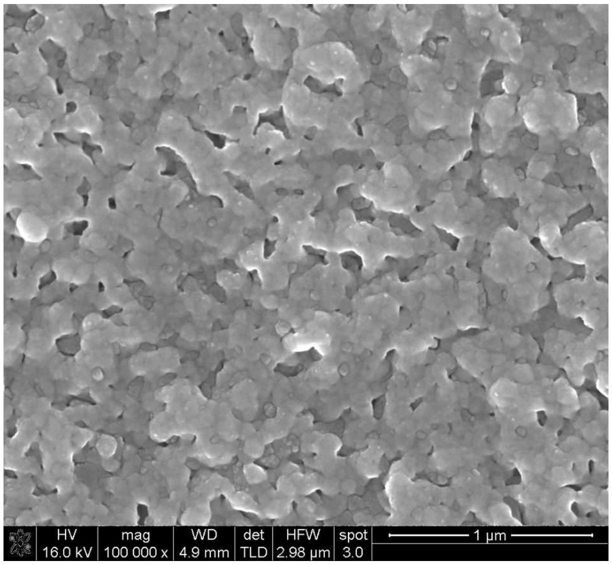

Figure 5. *Silver nanoclusters fused well with each other.*

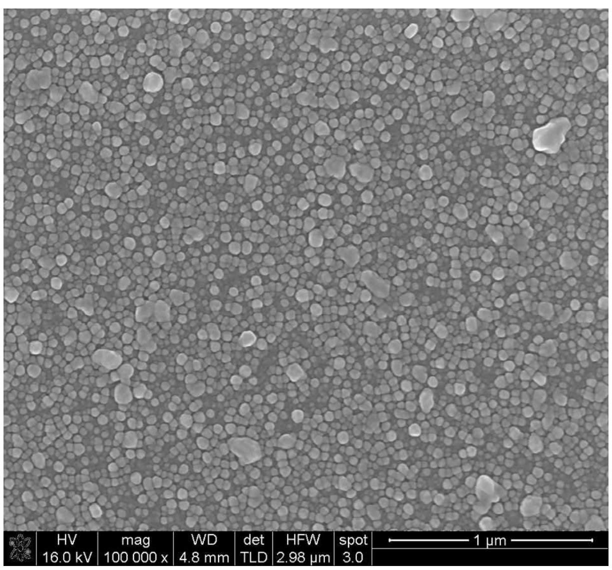

Figure 6. *Isolated silver nanoclusters due to the presence of the fusion control material.*

The line resistance was characterized with a digital multi-meter (Model 189, Fluke Corp., Washington, USA) and the measured line resistance values were 78.9, 38.3 and 24.8 Ω/cm when the electrode widths were 95.6, 136.7 and 190.1 µm, respectively.

Conclusions

In this study, a novel self-patterning technique is demonstrated and its fundamental mechanism is revealed. After laser-patterning the fusion control layer, which is composed of polyaniline granules, the metallo-organic silver solution was laid down and then hard-baked at 230 °C for 20 min. This thermal process converted metallo-organic silver into silver nanoclusters. In the absence of the fusion control material, silver nanoclusters are found fused well with each other and its sheet resistance is as low as 1.70±0.09 Ω/□. On the other hand, the fusion of silver nanoclusters is found inhibited by the fusion control material and its sheet resistance is as high as around 11.2±6.7 GΩ/□.

Unlike conventional approaches, efforts to precisely deposit conductive ink could be eliminated with this self-patterning technique. Instead, the two-step process, composed of (1) relatively easy removal step of the fusion control layer to prepare fine electrode regions and (2) rough deposition step of metallo-organic silver solution, will be utilized to self-differentiate conductive and non-conductive regions. In addition, this self-patterning technique provides an active means to prevent the short circuit formation.

Acknowledgements

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Author Biography

Dong-Youn Shin received his BS in mechanical engineering from Seoul National University (1997) and his MS and PhD in mechanical engineering (1999) and materials science (2003) from UMIST, UK. After a postdoctoral period at UMIST, he served at LG Chem Research Park to develop an inkjet printed color filter for TFT LCD and he is currently a senior research engineer at Korea Institute of Machinery and Materials. His research has focused on the theoretical and experimental analysis of the microfluidic behaviors in a piezo DOD inkjet print head and fine pattern generation for displays and electronics applications.