Research paper

Self-selective fine metal line coating using surface energy differences

Mu Kyeom Mun a, Doo San Kim a, Guen Young Yeom a,b,∗, Dong Woo Kim a,**

a Department of Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do, 16419, South Korea
b SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Gyeonggi-do, 16419, South Korea

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ABSTRACT

Self-selective coating is a new coating process that utilizes surface energy differences for metal ink coating. Hydrophilic and hydrophobic areas are defined on carbon black coated Polyimide (PI) substrate surface using atmospheric plasmas. At this state, when Ag ink is sprayed on PI, metal line is self-formed on hydrophilic surface due to its surface energy differences. As a result, an Ag ink line width of less than 6 μm could be formed on the PI surface after removing the carbon black. Due to the formation of the Ag line on the hydrophilic PI surface, the adhesion force of the Ag ink formed on the PI surface was ~64% higher than that of the Ag ink formed on the hydrophobic PI surface.

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1. Introduction

Electronic devices such as cellular phones, solar cells, touch screens, etc. require metal lines on the substrates or printed circuit boards to transmit electrical signals and transfer power [1,2]. These and these metal lines are generally formed using photolithographic patterning methods [3]. However, the formation of metal lines using conventional photolithographic patterning methods is complicated and expensive, requiring multiple process steps.

To replace this photolithographic patterning method, researchers have investigated various direct patterning methods including inkjet printing, screen printing, gravure printing, laser-induced thermal patterning, etc. [4–12]. In the case of inkjet printing, metal lines are formed using a non-contact method where metal ink is sprayed only on the area for a metal line. Therefore, metal lines can be formed economically with a small amount of metal ink and without damaging the substrate. However, there are several problems for fine line metal patterning, such as the adhesion of the metal line, spreading of the metal ink during inkjetting, difficulty in producing a high-resolution metal ink nozzle for inkjet printing [13–15]. For screen printing and gravure printing, metal lines can be formed only on specific areas, but the alignment of the printed metal line pattern has limited accuracy, and the formation of fine metal lines is also difficult due to the spreading of the metal ink, similar to inkjet printing. For direct patterning methods using a metal ink, a fine metal line pattern can form on the substrate by chemically treating the substrate surface to become hydrophobic. However, the hydrophobic surface of the substrate tends to decreases the adhesion of the metal line pattern [16,17]. Laser-induced thermal patterning can form highly accurate, fine multilayer metal line patterns on the substrates. However, due to the use of a high power laser, the cost of ownership is high and the substrate surface can be easily damaged during patterning.

This study investigates a self-selective metal line coating method that can be used to form fine metal line patterns on the substrates. The self-selective metal line coating method consists of coating a hydrophilic substrate with hydrophobically-treated carbon black, scratch patterning the carbon black with a micro tip, and spraying the substrate with a metal ink for selective metal line formation only on the scratch patterned area. The hydrophobic carbon black surface and the hydrophilic surface of the substrate were obtained via atmospheric pressure plasma (APP) treatment [18,19]. The APP was used for the surface treatments via in-line processing or roll-to-roll processing at a low temperature [28,29]. The self-selective coating of the metal ink was obtained by using the surface energy differences between the exposed hydrophilic substrate surface and the hydrophobic carbon black surface because the surface energy changes the surface properties, including the contact angle, adhesion, droplet roll off, etc. [20–27]. Especially, by using the self-selective coating, a fine metal line can be formed on the PI surface without using a conventional photolithographic patterning methods or without using an ink jet tools. The self-selective coating method investigated in this study is thought to be applicable to metal line formation on various substrates, including flexible substrates, with greater ease and at a lower cost similar to that of inkjet printing by forming a metal line only on a specific area and on a large substrate, but with a finer metal line pattern and with a higher adhesion strength because...
the metal line is formed only on the scratch patterned hydrophilic surface of the substrate.

2. Experimental

2.1. APP system and plasma treatment conditions

The schematic diagram of the APP system used in this experiment is shown in Fig. 1. The APP system consists of a dielectric barrier discharge-type system with two parallel electrodes. The top electrode (5 cm width × 23 cm length) was made from aluminum coated with 400 μm-thick Al2O3. The bottom electrode (10 cm width × 12 cm length) consisted of aluminum covered with 2 mm thick Al2O3 plates. The air gap between the two electrodes was maintained at 1 mm, and a 60 kHz quasi-pulse power (EN Power Electronics, Genius 10) was applied to the bottom electrode while the top electrode remained grounded. The operating gas mixtures were fed from the sides of the top electrode to the bottom electrode at an angle of 45° to obtain a uniform distribution of the process gas mixture.

150 μm-thick polyimide (PI, DuPont) was used as the substrate due to its high flexibility, strong chemical stability, and high thermal stability. The surface of the as-received PI was modified to become hydrophilic surface via treatment with He (10 slm)/O2 (2 slm) plasma generated with 5.5 kV for 1 min. To obtain a hydrophobic surface, the as-received PI surface was treated with He (10 slm)/SF6 (0.8 slm) at 5.5 kV for 1 min. The carbon black spray-coated on the PI surface was also treated with He (10 slm)/SF6 (0.8 slm) plasma for 1 min to make the carbon black surface more hydrophobic.

2.2. Carbon black and Ag ink coating

A spray coater (NTSEE, spray coater) with a spray gun (Puso Seiki, GP-2) and a heatable X-Y stage to ensure uniform coating was used to spray paint the carbon black on the PI surface. Carbon powder (Graphene Supermarket, Carbon Black) with diameter of 30 nm was used. The carbon black used in this experiment is not only very cheap ($50 per 100 g), but is also easily retrievable after spray-coating. Furthermore, its surface characteristics can be easily altered by treatment with plasma. For spray-coating, 0.5 g of carbon black were mixed in 500 ml of isopropanol (IPA) with a drop of dispersing agent (ALTANA, DISPERBYK-198). A sonicator (5510, Branson) was used to uniformly disperse the carbon black in the IPA. Then, the carbon black solution was spray-coated on the PI substrate at the X-Y stage while flowing N2 gas to the spray gun.

The metal ink used in this experiment is an Ag ink (PG-007, PARU). This Ag ink is solution containing 60 to 80 wt% of Ag nanospheres with 20 to 200 nm diameters. The ink had a viscosity of 47 cP and surface tension of only about 50 N/m. It could be mixed with deionized (DI) water to change the surface tension. The ink mixed with DI water was used in the experiment to increase the surface tension to roll off the ink on the carbon black surface during ink coating. The ink was soft baked on a hot plate for 15 min at 120 °C and then hard baked for an hour at 200 °C to form a solid Ag line pattern on the PI substrate.

2.3. Sample fabrication for adhesion test

It is very difficult to measure the adhesion force between the flexible PI substrate and the flexible Ag layer. Conventional methods to measure the adhesion force, such as the peel-off technique or pull-off technique, have limitations in that they change the interface area, propagate cracks out of the interface area, etc. during the test. To more accurately measure the adhesive force between the Ag layer and the PI substrate, the adhesion test used a sample with a shape as that shown in Fig. 2 [30, 31]. To measure the adhesive force, the Ag solution was spin coated on various PI substrates (as-is, hydrophilic treated, hydrophobic treated, etc.) with 2100 rpm in a spin-coater for 35 s, followed by soft baking on a hot plate for 15 min at 120 °C and then hard baking for an hour at 200 °C. A weak adhesive film (DAIO, ES5810) with a 6 mm-diameter hole was attached on the Ag surface to define the measuring area, and the open Ag/PI area was bonded with an epoxy with a PET string for the pull-off test. During the pull-off test, only the area defined by the opening of the weak adhesive film was pulled.

Fig. 1. Schematic diagram of the atmospheric pressure plasma (APP) system used in this experiment for the hydrophobic treatment or hydrophilic treatment of the polyimide (PI) substrate surface.

Fig. 2. Shape of the adhesion test sample used in the experiment for accurate adhesion force measurement between the Ag layer and PI substrate. For the adhesion force measurement, the Ag solution was spin coated on various PI substrates, followed by baking at high temperatures. A weak adhesive film with a 6 mm diameter hole was attached on the Ag surface to define the measuring area, and the open Ag/PI area was bonded with an epoxy with a PET string for the pull-off test. During the pull-off test, only the area defined by the opening of the weak adhesive film was pulled.
only the area defined by the opening of the weak adhesive film was pulled. This method allowed for a more accurate measurement of the adhesion force between the PI substrate and the flexible Ag layer without any alteration in the surface area by defining the areas of measurement more exactly and exhibiting no load drop and tail during the measurement.

2.4. Analysis and measurements

A contact angle analyzer (SEO, Phoenix 450) was used to investigate the change in the surface energy. The contact angles were measured after dropping an Ag solution droplet on the PI substrates (as-is, hydrophilic treated, hydrophilic treated, etc.) and hydrophobic, treated carbon black surface as a measure of the surface energy. The adhesion force between the PI substrate and the Ag layer was measured using a tensile strength tester (MECMESIN, Multi test 1-i). X-ray photoelectron spectroscopy (XPS, thermo VG SIGMA PROBE) was used to measure the chemical composition of the PI surface before and after the plasma treatment and the protected PI surface (PI surface exposed with a metal tip by removing the hydrophobic plasma-treated carbon black coated on the hydrophilic plasma-treated PI surface). The surface roughness and actual surface area per project area ratio was measured using an atomic force microscope (AFM, XE150-PSIA). An optical microscope was also used to observe the shape of the Ag line and to measure the width of the Ag line formed on the PI surface by the self-selective coating method.

3. Results and discussion

Fig. 3 shows a schematic diagram of the sequence to coat the self-selective metal ink line on the PI substrate. As shown in Fig. 3, the following procedure was used to form the self-selective metal ink line. (a) The substrate was first treated with He/O₂ atmospheric pressure plasma to form a hydrophilic surface. (b) The hydrophilic treated PI surface was then spray-coated with a carbon black solution. (c) The PI substrate coated with the carbon black was treated with He/SF₆ plasma for hydrophobicity. (d) The carbon black surface was scratch written with a fine line to expose the hydrophilic PI surface under the carbon black using a metal tip. (e) On the scratch written PI surface coated with carbon black, an Ag ink was sprayed (or dropped). (f) Finally, the substrate was annealed on a hot plate for 15 min at 200 °C to solidify the Ag ink on the PI surface exposed by the metal tip, and the carbon black covering the remaining PI surface was removed by dipping in alcohol and sonicking for 1 min, exposing the fine Ag line.

To ensure self-selective coating, significant differences in the surface energy between the PI surface and the Ag ink are required [32]. The surface of the PI substrate needs to be hydrophilic to improve the adhesion of the Ag ink, and the carbon black surface needs to be hydrophobic to ensure the roll-off of the Ag ink dropped on it [33]. Fig. 4 shows the optical images of an Ag solution droplet (a) on the hydrophilic treated PI substrate and (b) on the hydrophobic treated carbon black layer. The Ag solution droplet on the surface of the PI substrate showed a very low contact angle, indicating a hydrophilic surface, and the Ag solution droplet on the carbon black layer surface showed a very high contact angle, indicating a hydrophobic surface (Fig. S1, S2).

In fact, the Ag ink dispersed in an organic solution, such as ethylene glycol, glycerol, alcohol, etc., has a very low surface tension [34,35]. Therefore, it is difficult to obtain significant differences in the surface energies with any surface to carry out self-selective coating. Therefore, the Ag ink solution was mixed with DI water to increase its surface energy. Fig. 5 (a) shows the contact angle of the Ag ink solution as a function of the mixture ratio of the Ag ink and DI water on the hydrophilic plasma treated PI surface and the hydrophobic plasma treated carbon black surface (Fig. S3). For the PI surface, 100% Ag ink solution showed a contact angle of about 16°, and the 100% DI water showed a contact angle of about 50°. The increase in DI water percentage in the Ag ink mixture increased the contact angle from about 18° for the 80% Ag ink solution to 41° for the 20% Ag ink solution. When the contact angle of the Ag ink mixture was measured on the hydrophobic plasma treated carbon black surface, the contact angle was significantly higher at about 137° for the 100% Ag ink, and the increase in the DI percentage in the Ag ink mixture increased the contact angle further to about 145° for the 80% Ag ink mixture. However, when the Ag ink percentage in the Ag ink solution was lower than 70%, the ink no longer stayed on
the carbon black layer surface and rolled-off. Therefore, no contact angle could be measured [36]. The Ag ink mixture used for self-selective coating needs to show a high adhesion force and narrow Ag line widths on the PI substrate after coating. In general, the Ag ink with a higher contact angle on the substrate has a lower adhesion force. Therefore, to obtain a higher adhesion force on the PI substrate surface while rolling off on the carbon black layer surface during Ag ink coating, a 70% Ag ink mixed with 30% DI water was used, showing the smallest contact angle with the PI substrate and also allowing the roll-off on the hydrophobic carbon black ink. The Ag ink can roll-off on the carbon black surface when the surface roughness is high enough for Cassie-Baxter model (where, the solution is located above the textured surface without wetting) [37]. However, as shown in Fig. 5(b), the rms surface roughness of our carbon black after coating on the PI surface (and regardless of hydrophobic treatment) was about 1.54 μm which is less than minimum 2.0 μm height of surface texture for Cassie-Baxter model [37]. Therefore, it is believed that the roll-off of Ag ink observed in Fig. 5(a) is related to the hydrophobic properties of the carbon black surface. Fig. 5(c) shows the AFM roughness of the scratch written PI surface after the carbon black coating. As shown in the figure, the scratch written PI surface was also smooth similar to that of carbon black surface. However, the hydrophobic PI surface is exposed by the scratch writing because the hydrophobic carbon black was removed, therefore, the scratch written PI surface can be filled with Ag ink while the Ag ink is rolled off on the carbon black coated surface during the Ag ink coating.

The hydrophobic plasma-treated carbon black layer surface was scratch written with a micron scale tip with a size of 6 μm to expose the underlying hydrophilic plasma treated PI surface, and 70% Ag ink solution was coated on the surface. Fig. 6(a) shows an optical image of a valley with a width of ~5.64 μm that formed on the carbon black layer coated PI substrate by scratch writing with a 6 μm width micron scale tip. After scratch writing, the 70% Ag ink mixture was sprayed (or dropped) to form the Ag ink line only in the valley that formed on the PI substrate. Fig. 6(b) shows an optical image for the Ag line that formed on the PI substrate surface after annealing the Ag ink coated PI substrate and following the removal of the carbon black layer. The Ag line had a width of ~5.88 μm. Therefore, the self-selective coating method can be used to form a metal line as narrow as 6 μm, which is difficult to achieve with conventional direct ink printing methods. The width of metal line was changed with the scratching writing force and the line width was varied from 2 μm–50 μm by varying the force of the scratch writing. In Fig. 6, we are showing only a short line because it is difficult to control the scratch writing force. It is believed that, by installing a pen-writing system instead of a hand-writing, more controlled, much longer, and complicated metal lines can be written.

For the Ag line formed on the PI substrate, both the formation of a fine line and a high adhesion force on the substrate are required. The adhesion strength of the 70% Ag ink was investigated by blank-coating the various PI substrate surfaces, and the results are shown in Fig. 7. The Ag ink was coated on the various PI substrates including as-received PI, hydrophilic plasma treated PI (not on carbon black surface), hydrophobic plasma treated PI (with the same recipe as the hydrophobic plasma treatment for carbon black), and protected PI substrate (the PI surface was exposed by peeling off the hydrophobic plasma treated carbon black layer covered on the hydrophilic plasma treated PI substrate; similar to the PI substrate area exposed by scratch writing with a micron scale tip during self-selective coating). The Ag inks coated on the various substrates were also annealed using the method shown in the experimental section. To accurately measure the adhesion strength, ten samples were measured for each condition, and the average values were calculated for the figure. As shown in Fig. 7, the adhesion strength of the Ag layer formed on the hydrophilic plasma treated PI substrate obtained with He/O2 plasma treatment increased by approximately 30% when compared to that on the as-is PI substrate. However, when the PI substrate was hydrophobic plasma treated with the He/SF6 plasma, the adhesion force decreased by approximately 22% compared to that on the as-is PI substrate. The adhesion strength of the Ag layer formed on the protected PI substrate was similar to that formed on the hydrophilic plasma treated PI substrate. Therefore, the Ag line formed via self-selective coating can have a similarly high adhesion strength as that formed on the hydrophilic PI substrate while keeping a fine Ag line during coating. In addition, if the adhesion strength of the Ag layer on the protected PI surface is compared to that formed on the hydrophobic plasma

![Fig. 5](image-url) (a) Contact angle of the Ag ink solution measured as a function of the mixture ratio of the Ag ink and DI water on the hydrophilic plasma treated PI surface and the hydrophobic plasma treated carbon black surface. (b) Surface roughness of PI after carbon black coating. (c) exposed PI surface.
treated PI surface for the fine Ag line formation, an increase of about 64% in the adhesion strength can be expected.

The composition of the PI substrate surfaces obtained with various treatments, as shown in Fig. 7, was investigated using XPS, and the results are shown in Table 1. For the as-is PI substrate, the surface was observed to be mostly composed of carbon, oxygen, and nitrogen (hydrogen cannot be measured using XPS), which is similar to the bulk composition of polyimide (carbon 69%, oxygen 21%, nitrogen 7.4%, and hydrogen at about 2.6%). After treating with hydrophilic He/O₂ plasma, the carbon percentage decreased with an increase in oxygen while maintaining a similar nitrogen percentage. For the hydrophobically treated PI substrate, the oxygen percentage decreased with an increase in nitrogen while maintaining a similar carbon percentage. For the hydrophilically treated PI surface with He/SF₆ plasma, a fluorine percentage of 37.7% was observed on the PI surface with a decrease in carbon, oxygen, and nitrogen on the surface. Therefore, the hydrophilic surface of the He/O₂ plasma treated PI surface is related to the oxygen bonded on the surface, which increases the surface energy of the PI surface. In contrast, the hydrophobic surface of the He/SF₆ plasma treated PI surface is related to the carbon-fluorine polymer that formed on the PI surface with a decrease in the surface energy of the PI surface. For the protected PI, a small amount of fluorine was observed on the surface, which was possibly due to the diffusion of fluorine through the carbon black layer during the treatment with He/SF₆ plasma on the carbon black coated PI substrate, possibly increasing the hydrophobicity of the PI surface. However, possibly due to the high percentage of oxygen on the PI surface, similar to the hydrophilic plasma treated PI surface, the protected PI showed a similar adhesion strength with the Ag layer as the hydrophilic plasma treated PI surface.

4. Conclusions

This study investigated a direct printing method for fine Ag lines on flexible substrates, such as polyimide (PI), by using an Ag ink, a self-selective coating method exploiting the difference in surface energy between the surfaces (PI surface and carbon black surface) and ink. The high differences in surface energy between the surfaces and Ag ink were obtained by treating the PI substrate with a He/O₂ plasma to obtain a hydrophilic surface coated with a carbon black layer and coating the carbon black layer surface with a He/SF₆ plasma to obtain a hydrophobic surface. The Ag ink was also mixed with DI water to obtain a higher surface energy. The hydrophilic PI substrate surface was exposed by direct scratch writing on the carbon black layer surface with a micron size tip. When the Ag ink was uniformly sprayed on the scratch written PI substrate, only the hydrophilic PI surface exposed by the tip was coated with Ag ink due to the surface energy differences, and the ink on the remaining hydrophobic carbon black surface rolled away. This resulted in the formation of a fine Ag line with a width of less than 6 μm. The Ag line was coated only on the hydrophilic PI surface, and a comparison with the Ag line formed on the hydrophilic PI surface reveals a high adhesion strength for the Ag line on the PI substrate of about 64% higher than that formed on the hydrophobic PI surface. In addition, a fine Ag line was formed. The self-selective coating method is believed to be applicable to metal inks and to many other organic inks for to form fine lines via direct patterning with a high adhesion strength to the substrate.

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