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Research paper

Self-selective fine metal line coating using surface energy differences

Mu Kyeom Mun [a], Doo San Kim [a], Geun 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. Hydrophobic and hydrophilic 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.

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 inkjeting, 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

* Correspondence to: G.Y. Yeom, SKKU Advanced Institute of Nanotechnology(SAINT), Sungkyunkwan University, Suwon, Gyeonggi-do 16419, South Korea.
** Corresponding author.
E-mail addresses: gyyeom@skku.edu (G.Y. Yeom), dwkim111@gmail.com (D.W. Kim).

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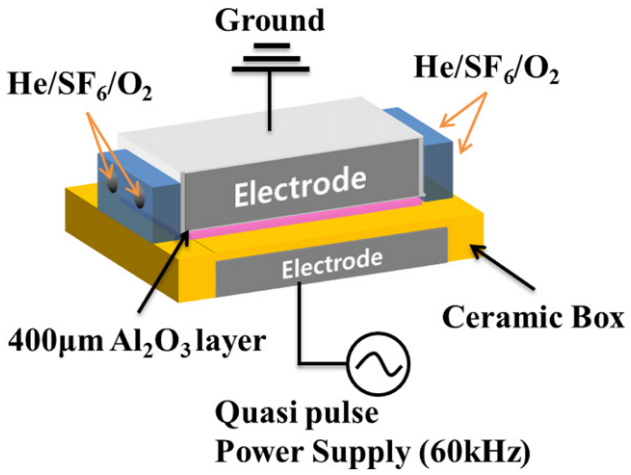

Fig. 1. Schematic diagram of the atmospheric pressure plasma (APP) system used in this experiment for the hydrophobic treatment or hydrophilic treatment of the polyimide (PI) substrate surface.

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 Al_2O_3. The bottom electrode (10 cm width × 12 cm length) consisted of aluminum covered with 2 mm thick Al_2O_3 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)/O_2 (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)/SF_6 (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)/SF_6 (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 (Fuso Seiki, GP - 2) and a heatable X-Y stage to ensure uniform coating was used to spray coat 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 N_2 gas to the spray gun.

The metal ink used in this experiment is an Ag ink (PG-007, PARU). This Ag ink is a 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 was 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 polyethylene terephthalate (PET) string for the pull-off test. During the pull-off test,

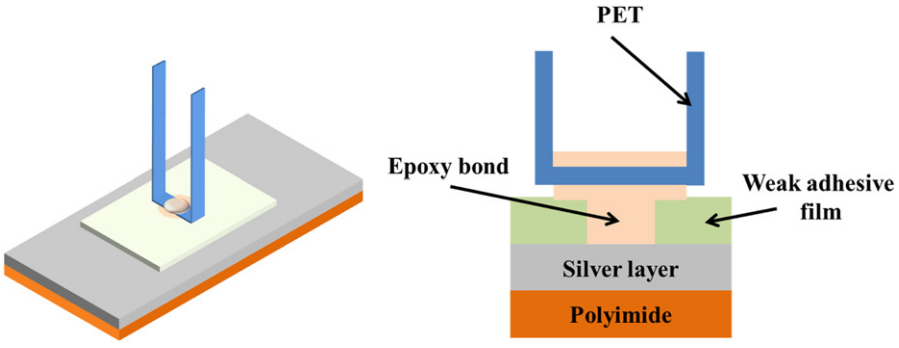

Fig. 2. Shape of the adhesion test sample used in the experiment for accurate adhesion force measurement between the Ag layer and PI substrate. For the adhesion force measurement, the Ag solution was spin coated on various PI substrates, followed by baking at high temperatures. A weak adhesive film with 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.