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Direct Writing Patterns for Electroless Plated Copper Thin Film on Plastic Substrates

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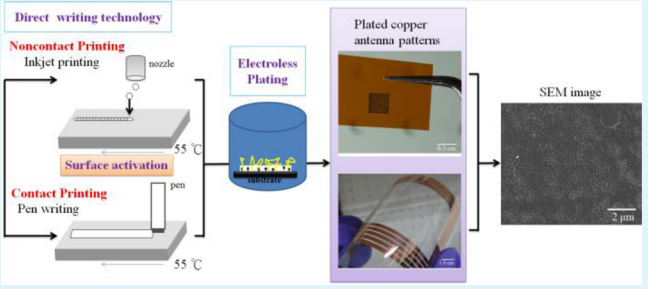
ABSTRACT: A simple and efficient method is developed to create conductive copper thin films on polymer surfaces. Instead of regular palladium colloid inks, micropatterns of silver nitrate inks, which serve as an activating agent for copper plating, were printed and dried on flexible plastic substrates. The printed plastic sheets were then immersed in an electroless copper plating bath at 55 °C for 2 min to create copper thin films on the printed patterns. The prepared copper films have an electrical conductivity as high as 83% of bulk copper and show good adhesion on PET or PI substrates.



KEYWORDS: *copper thin film patterns, electroless plating, silver ion ink, inkjet printing, pen writing, plastic substrates*

INTRODUCTION

Printed electronics has provided a new fabrication method for flexible, low-cost, and lightweight electronic devices, such as smart label and flexible display.[1−3] For the so-called "printed electronics," solution-based electronic materials, such as metal nanoparicles and inorganic semiconductors, are printed on plastic sheets to create flexible microelectronic circuits. Metals, such as gold and silver, have been widely adopted in these printed devices to serve as conductive parts. Because of the low price and high electric conductivity, copper has recently attracted wide attention in printed conductive features. At present, most commonly used conductive copper inks are nanoparticle suspensions with plastic binders.[3−7] The as-printed patterns usually have a large resistivity and require a one-hour sintering process at a temperature of 200 °C to reduce the resistivity down to 2.2 times of that for bulk copper.[3] Because most plastic substrates might melt at high temperatures, the sintering process for nanoparticle inks has limited the choice of substrates. Thus, alternative synthetic approaches, such as metallo-organic decomposition (MOD),[8−10] are currently of research interests for metal patterns on polymer substrates.[11−14]

An alternative synthetic route for patterning conductive copper thin films on plastic surfaces at low temperatures is electroless plating.[15−18] The general process of electroless plating involves (i) surface preparation, (ii) surface activation by seeding catalytic metal particles on plated surfaces, and (iii) electroless plating bath to recover copper on the activated surfaces. By controlling the position of activation layers, one can easily determine where the copper crystals grow and create copper thin film patterns. Liquid deposition methods, such as microcontact printing[19−21] and inkjet printing,[22−25] are commonly used to print palladium (Pd) colloid inks on polymeric substrates before subsequent copper electroless plating.[19,20,22,23] This synthetic route creates highly conductive copper micropatterns on polymeric surfaces for flexible circuits at low temperature with great processability. Recently, silver colloid is also found to be useful in the electroless copper plating instead of conventional Pd colloid.[26,27] Although the silver-based materials provide cheaper Pd-free catalysts for copper plating, challenges remain on how to remedy plastic surfaces efficiently for silver-related activating agents.

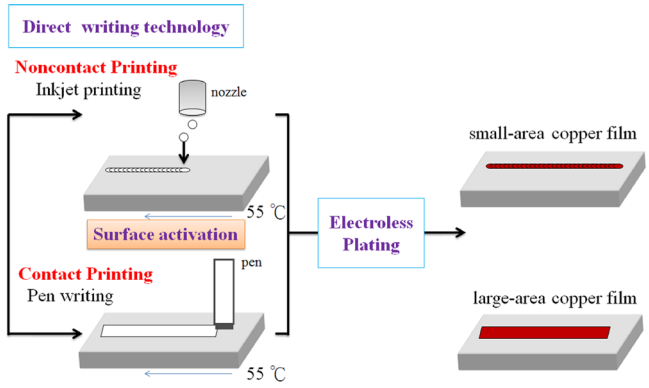


Figure 1. Schematic diagrams of the metallization process: inkjet-printed or pen-written activating patterns following by electroless copper plating.

In this work, we present a simple and fast process to synthesize conductive copper patterns on plastic substrates by combining inkjet printing and electroless plating methods. First, a particle-free silver nitrate ink was printed on polyethylene terephthalate (PET) or polyimide (PI) films as an activating agent for copper plating. The printed samples were subjected to electroless plating to create highly conductive copper patterns. In addition, the activation patterns can also be generated by a contact printing method with the same silver ink. This synthetic approach can be further extended for mass production when a large-area of Cu patterns is required.

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EXPERIMENTS

The silver ion ink was prepared by adding 3 mM silver nitrate (Mallinckrodt Chemicals Inc., USA) in a solvent mixture, which contained ethanol/ethylene glycol/DI water in a ratio of 85:5:10 vol%.

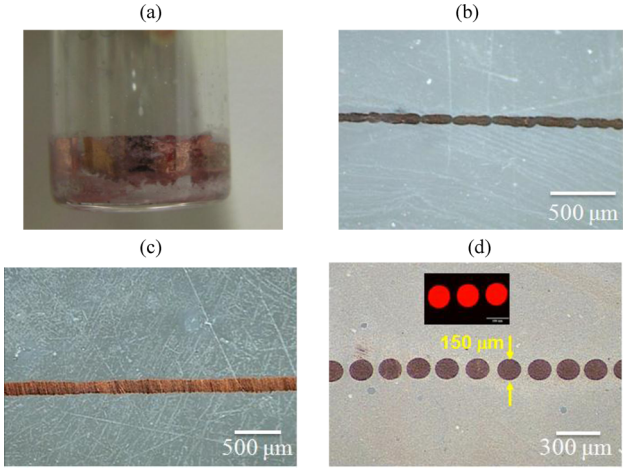

Figure 2. (a) Electroless plated copper thin film created by rinsing the glass bottle with aqueous silver nitrate solution (3 mM) at room temperature. (b) Plated copper thin films on PET by printing a silver ion ink (3 mM $AgNO_3$ in 95 vol % ethanol). (c) Same as (b), but the solvent is replaced by ethanol:DI water:ethylene glycol =85:5:10 vol %. (d) A comparison between the as-printed dots and those after copper plating. The inset picture shows the dots from rhodamine-containing ink under fluorescence microscopy.

The viscosity and surface tension of the silver nitrate ink at 25 °C were 1.73 cP and 29.0 mN/m, respectively, and had a contact angle of 10 degrees on PET sheets (Universal film, Japan). The PI films were purchased from InTech Materials Co., Taiwan. Before printing, the silver nitrate ink was filtered with a 0.45 μm filter (HP045AN, Advantec, USA) to remove airborne particles. The copper bath solution contained 2.704 g of $CuSO_4 \cdot 5H_2O$ (Sigma Aldrich, USA), 8.15 g of sodium potassium tartrate (J. T. Baker), 3.25 g of NaOH (Mallinckrodt Chemicals Inc., USA), 0.1 L of DI water, and 25 mL of an aqueous solution of glyoxal (40 wt.%, Alfa Aesar, USA). The printed samples were dried on a hot plate at 55 °C for 2 min in atmospheric pressure to evaporate organic solvents. The electroless plating of copper was then performed by immersing the printed samples in copper bath at 55 °C.[28] The synthesized copper films were then rinsed with DI water, and dried at 70 °C in a vacuum oven. Figure 1 shows a diagram of this process.

The drop deposition was made by MicroFab JetLab4 system (MicroFab Inc., USA). The thickness of the synthesized copper films was determined by surface profilometry (Veeco Dektak 6M). The crystalline structure of the copper films was measured with X-ray diffractometer (Rigaku Ultima IV). Microstructures of plated films were examined with scanning electron microscopy (Nova NanoSEM 230).

RESULTS AND DISCUSSION

Ink Formulation. Silver nitrate inks activate PET surfaces and help the creation of plated copper thin film patterns with well-defined boundary. Figure 2 shows the effects of ink formulation on plated copper patterns. From the literature,[29] glass surface can be activated after rinsing with a 3 mM aqueous silver nitrate solution. A so-called "copper mirror" reaction can then be triggered on the activated area in the copper plating

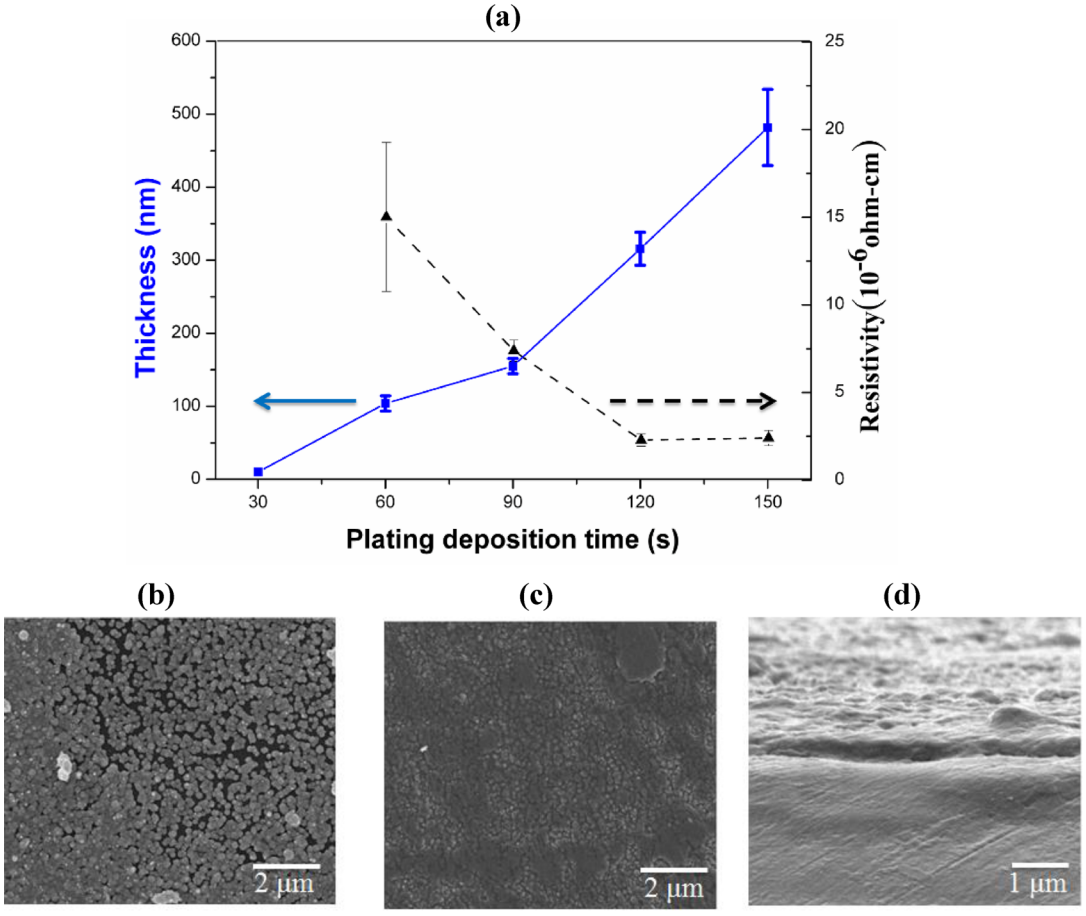

Figure 3. (a) Thickness and resistivity of plated copper thin films versus the immersion time in copper plating bath. (b) The SEM image of deposited copper thin films after 60s deposition. (c) Same as b, but with a 120 s deposition. (d) The cross-sectional profile of c.

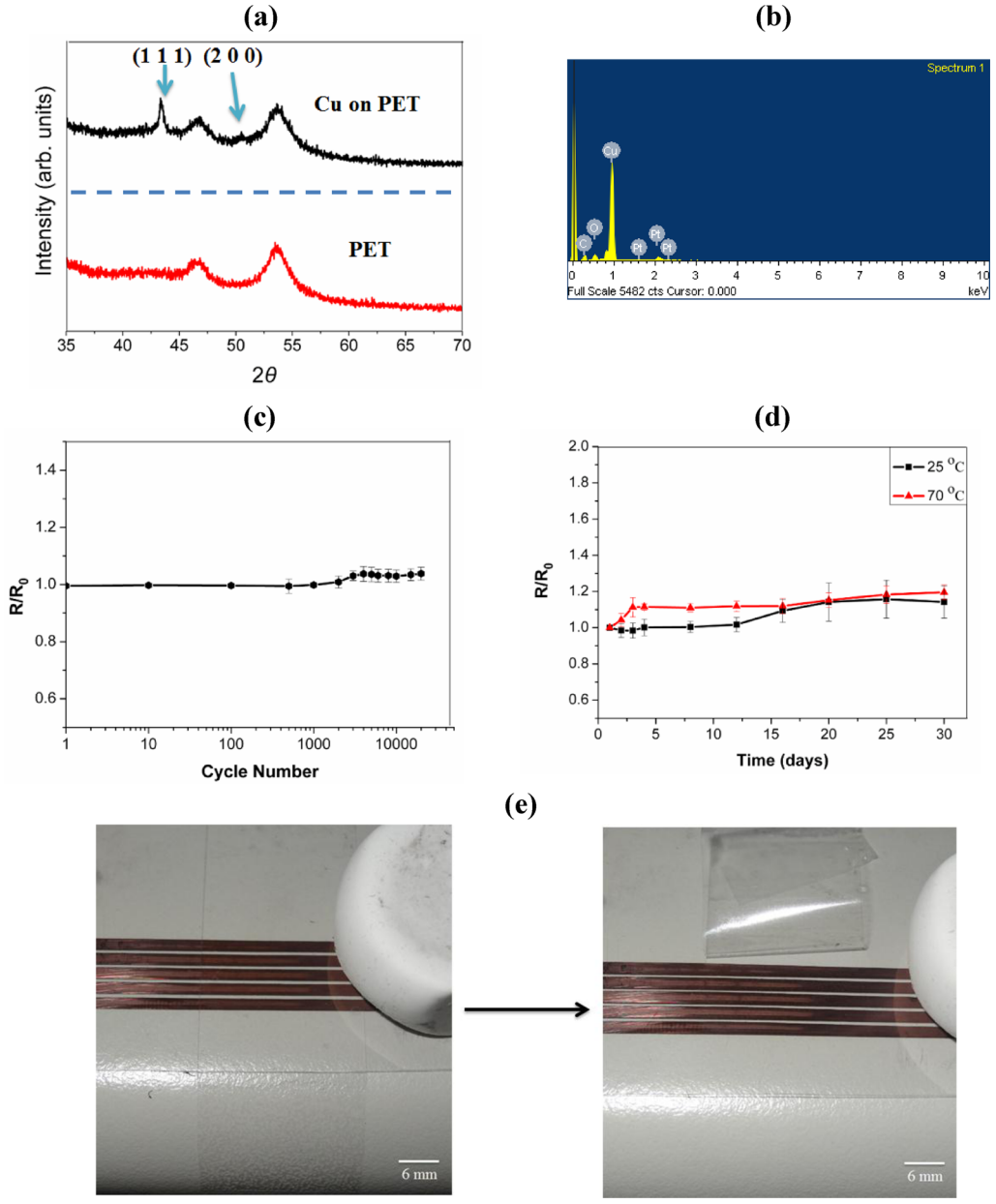

Figure 4. (a) XRD pattern and (b) EDX spectrum for plated copper thin films. The resistance increase ratio (R/R_0) of plated copper tracks under (c) bending performance test and (d) long-term storage test. (e) A simple tape test for plated copper thin films.

bath (Figure 2a). The plated copper thin films attached to glass firmly and showed a shiny red color. To apply the same approach on PET, a hydrophobic substrate, organic solvents, such as ethanol, are required to help the ink wettability. First, 3 mM $AgNO_3$ dissolved in 95% ethanol was printed on PET. Because of the fast evaporation rate of ethanol, this ink left discontinuous traces after inkjet printing (Figure 2b). Addition of ethylene glycol, which has a higher boiling point at ~200 °C, can reduce the evaporation rate and greatly improve morphological control of the printed patterns (Figure 2c).[30] The inkjet-printed patterns and those after electroless copper plating were also compared. Because the silver ion ink was transparent and invisible after printing, Rhodamine (1 ppm) was added into the ink for the convenience of observation. Results showed that the as-printed dots (red dots in the inset picture in Figure 2d) had the same diameter and dot spacing as those after copper plating, indicating that the copper patterns only grow on the printed area.

Deposition Time in Electroless Bath. Figure 3a shows the copper layer thickness versus deposition time in the plating bath at 55 °C. A printed line of 150 μm as shown in Figure 2c was used to test the deposition thickness. With a short deposition time of 30 s, the synthesized copper film was too thin and the resistance was too large to be measured. As the deposition time increased to 60 or 90 s, the plated films showed red shiny color with average film thickness of 100 to 155 nm. After cleaning and drying, the resistivity of the plated copper tracks is 3−6 times of bulk copper. This large resistance results from the incomplete copper coverage on PET surfaces. Figure 3b shows the SEM image of a plated Cu film after 60s deposition. The synthesized copper films had a loose microstructure packed with scattered nanoparticles of 100 to 150 nm. To reduce the resistance, the deposition time was extended to 120s to synthesize a thicker copper film of 300 nm with a dense and continuous microstructure (Figure 3c). The growth in copper

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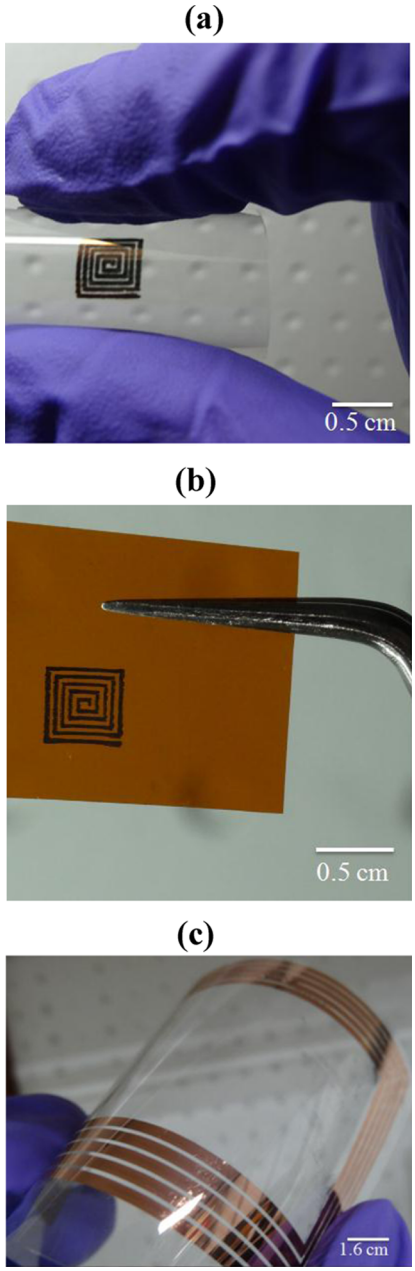

Figure 5. Plated copper antenna from inkjet-printed patterns on (a) PET and (b) PI sheets. (c) Plated copper films from written patterns with a whiteboard marker pen. All the patterns were created with the same silver nitrate ink.

film leads to a more compact grain packing, and reduces the electron transfer barrier.[31] As a result, the resistivity drops to 2.08 ± 0.21 μ Ω cm, which is about 1.2 times of the bulk copper. The cross-sectional view of the same film (Figure 3d) also reveals the formation of a dense continuous 300 nm thick film after 120 s deposition. For deposition longer than 120 s, the film thickness increases but the resistivity remains the same. Thus, a 120 s deposition time was used for the examples in the following sections.

Basic Elemental Analysis and Mechanical Stability. X-ray diffraction is used to probe the crystalline structures in the printed samples. Figure 4a shows XRD patterns of copper films deposited on PET. Two characteristic peaks for metallic copper crystalline at 44 and 50° are present for the Bragg's reflection indices of (111) and (200) planes in FCC structure. To further identify the chemical composition of the printed samples, energy-dispersive X-ray (EDX) spectrum analysis was also performed. The results (Figure 4b) confirmed the existence of copper with some other elements in the PET substrate, such as C and O elements.

The plated copper thin film patterns show good adhesion on PET. Continuous and uninterrupted copper thin lines of 150 μm in width were used to test the mechanical and chemical stability. Figure 4c shows change in samples resistance after repeated bending[32] as function of the number of bending cycles. The resistance increase ratio (R/R_0) rises only slightly (~ %) after being bent repeatedly for more than 10000 bending cycles. This gradual loss of conductivity occurs with bending cycle, and could attribute to the grain defects of films under compression.[32] The chemical stability has also been tested by measuring the resistance variation of plated thin films in 30 days. Although the resistance of the samples increased rapidly by 20% at 70 °C in 3 days, it plateaued afterward for the next 27 days. When stored at room temperature or a lower oxidation rate, the same plateau was reached after 20 day storage, indicating that the surface oxidation might create a protection layer for the copper thin films. A tape test was also performed to test the adhesion of plated copper films after storage. As shown in Figure 4e, the copper films completely remained on the plastic surfaces after removing the attached tape (Scotch Cat. 600 tape, 3M), indicating the great adhesion between the plated copper films and PET surfaces.

Direct Writing Patterns. Copper patterns can be plated on flexible substrates with the same silver ion ink by either inkjet printing or pen writing methods. Figure 5a shows a photograph of an RFID antenna created by electroless copper plating with inkjet-printed patterns. The antenna has a line width of 250 μm on a 5 × 5 mm^2 PET sheet. Same pattern can also be created on polyimide PI surfaces (Figure 5b). To show the ability of this synthetic route for large scale copper thin films, an example of contact writing methods was also demonstrated here. A blank whiteboard pen was soaked in the silver ion ink for 30 min, and was used to plot a large antenna pattern on a PET sheet with a regular pen plotter. Next, the plotted samples were placed in copper bath to create copper patterns of centimeter scales as shown in Figure 5c. The plated copper films also showed well-defined boundaries with great conductivity and adhesion on PET. This pen writing method provides a simple metallization process and can be further extended to create conductive patterns on three-dimensional objects.

■ CONCLUSIONS

In conclusion, a simple and efficient method is developed to synthesize copper thin films on plastic sheets. Instead of regular palladium colloid inks, micropatterns of silver nitrate inks, which serve as an activating agent for copper plating, were printed on flexible substrates. The printed plastic sheets were then immersed in an electroless plating bath at 55 °C for 2 min to create copper thin films on the printed patterns. The prepared copper films have an electrical conductivity as high as 83% of bulk copper and show good adhesion on PET or PI substrates. One can also write patterns of catalytic silver nitrate inks directly on the surfaces and create copper thin films with electroless plating method. This method shows a fast synthetic route for copper patterns with dimensions ranging from micrometers to centimeters and opens an avenue for potential applications in printed electronic devices.

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Notes

The authors declare no competing financial interest.

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