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Fabrication of Gold Patterns via Multilayer Transfer Printing and Electroless Plating

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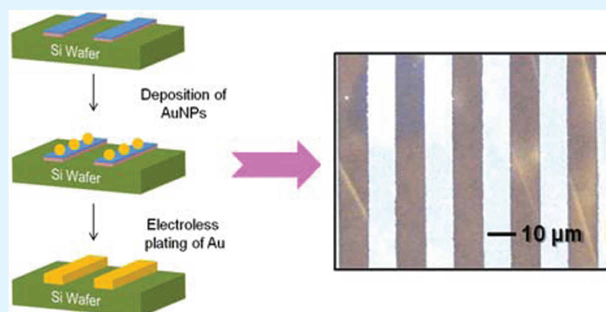
S Supporting Information

ABSTRACT: Gold patterns were fabricated on Si wafer substrate via multilayer transfer printing of polyelectrolytes, followed by selective deposition of gold nanoparticles (AuNPs) and then electroless plating of gold. First, PDMS stamp was coated with $(PAH)_1/(PSS/PDAC)_{10}$ multilayer system, followed by transfer printing on the piranha cleaned fresh Si wafer substrate. Next, the substrate was dipped in AuNP solution for deposition of the nanoparticles on PAH layer. Then, the substrate was subjected to electroless plating to obtain the gold patterns. Very clean and precise gold patterns with electrical conductivity of $2.5 \times 10^5\ \Omega^{-1}\ cm^{-1}$ were obtained.



KEYWORDS: *gold pattern, multilayer transfer printing, polyelectrolyte, gold nanoparticle, electroless plating, electrical conductivity*

■ INTRODUCTION

Microfabrication of electronic components, including low resistance metal electrodes and interconnects on various surfaces with high resolution is an essential element in the fabrication of electronic as well as optoelectronic devices.[1,2] Metals such as gold, silver, nickel, and copper have been utilized in the electronics industry, but gold has attracted attention because of its chemical inertness and high conductivity.[3] Photolithography is the mainly utilized fabrication technique in microelectronics industry.[4] However, it is known to be an expensive, complicated, and time-consuming process.[5] Thus, various nonconventional lithography techniques have been introduced such as microcontact printing (MCP),[6−8] nanoimprinting[9,10] and inkjet printing.[11,12] Among the mentioned methods, MCP has received great attention, because of its simplicity, low-cost, high-throughput, and capability of high speed patterning on large areas.

Consequently, numerous approaches have been developed to prepare gold patterns by utilizing MCP technique. For instance, the Whitesides group[6] demonstrated the fabrication of gold patterns by MCP of alkanethiol on gold-coated substrate, followed by wet chemical etching. Unfortunately, this approach needs expensive and complicated metal evaporation equipment and includes toxic etching materials. Then, the Rogers group[7] introduced the nanotransfer printing method, which relies on MCP of gold-coated PDMS stamp on the thiolsilane modified substrate. This method produced nice gold patterns, but there is a need for sophisticated thermal evaporator system with collimated flux to inhibit deposition on the sidewalls of the stamp, and thus only 20 nm thickness of gold could be printed. Furthermore, Wu[8] has shown another approach including MCP of alkanethiol-capped gold nanoparticles (AuNPs), followed by low temperature sintering in order to fabricate gold patterns. However, with this approach, it is not easy to tune the thickness of gold patterns with smooth surface and afford good adhesion to the substrate.

Recently, electroless plating has drawn great attention in the microelectronic industry because it does not require any expensive and sophisticated equipment and it is easy not only to tune the metal thickness but also to obtain smooth surface.[13] Consequently, MCP has been successfully combined with electroless plating for preparation of metal patterns.[14−19] For instance, Carmichael group[14,15] synthesized novel oligomers and patterned them on glass and polymer substrate via MCP, followed by selective binding of colloidal catalyst and electroless plating of copper or nickel. Nice metal patterns with good fidelity were obtained but this approach needs special synthesis skills and thus, it is not industrally applicable. In addition, Aldakov[16] reported the preparation of copper patterns, which relies on MCP of alkanedithiol on gold substrate, and then deposition of palladium catalyst and electroless plating. However, this approach is limited for metal substrates so it can not be utilized for silicon, glass or polymer substrates. Moreover, Yoon[17] demonstrated fabrication of gold patterns on polyimide substrate via MCP of KOH solution, followed by selective binding of palladium ion and electroplating of nickel or gold. This approach depends on the surface modification of the substrate by the alkali hydrolysis and thus, it could be only utilized for polyimide substrate. Hsu[18] and Mewe[19] prepared silver patterns via MCP of silane coupling agents, followed by electroless plating of silver. Unfortunately, clean metal patterns could not be achieved with

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this approach. This was attributed to the low molecular weight of silane coupling agent, which resulted in gas phase deposition and lateral diffusion of the molecules, and thus metal deposition in the nonstamped region. Therefore, high-molecular weight species such as dendrimers and polymers are preferred over small molecules for precise patterning with MCP technique.[20] On the other hand, Hammond group[21] introduced multilayer transfer printing (MTP), which includes MCP of polyelectrolyte coated PDMS stamp on polyelectrolyte coated substrate. This technique successfully provided precise and functional polymer patterns without any lateral diffusion on silicon as well as polymer substrates. Then, this approach was utilized for patterning of polymer composite films,[22] CNT multilayer film,[23] optically active materials,[24] and bionanocomposite films.[25] However, it has never been utilized for fabrication of metal patterns.

In this study, therefore, it was attempted to fabricate clean and highly conductive gold patterns on Si wafer substrate via multilayer transfer printing with PDMS stamp, followed by selective deposition of AuNPs and electroless gold plating. First, the Si wafer substrate was cleaned with piranha solution to generate hydroxyl moieties. Second, PDMS stamp was coated with $(PAH)_1/(PSS/PDAC)_{10}$ multilayer system, followed by multilayer transfer printing on the substrate. Next, the substrate was dipped in AuNP solution for selective deposition of the nanoparticles on PAH layer. Finally, the substrate was subjected to electroless plating to obtain the gold patterns.

MATERIALS AND METHODS

Materials. $HAuCl_4$, $Na_3C_6H_5O_7$, NH_2OH, poly(diallyldimethylammonium chloride) (PDAC, MW = 100 000−200 000), poly(sodium 4-styrenesulfonate) (PSS, MW = 100 000) and poly(allylamine hydrochloride) (PAH, MW = 70 000) were purchased from Sigma-Aldrich (St. Louis, USA) and used as received. Polished test-grade Si wafers (100) and glass slides were cut into 15 × 15 mm^2 size, sonicated in acetone and ethanol for 15 min and cleaned with piranha solution (7:3 H_2SO_4/H_2O_2) at 90 °C for 1 h. ***Caution:*** *Piranha solution is strong oxidant and should be handled with care.* Then, they were rinsed with DI water for several times and dried under nitrogen flow. Negatively charged hydroxyl moieties (−OH) were generated on the substrate by piranha cleaning. The substrates were immediately used after cleaning in order to prevent contamination. Poly(dimethylsiloxane) (PDMS) was obtained from Dow Chemical and used for preparing stamps on the silicon master by curing at 60 °C for 5 h.[21] Then, the stamps were sonicated in hexane and ethanol for 20 min to remove low MW oligomers.[2] Flat stamp was used for condition optimization whereas glass slides were utilized as substrates for optical property measurement.

Synthesis of Gold Nanoparticles. Citrate capped AuNPs (12.9 ± 1.5) were synthesized by following the standard citrate reduction method.[26] The AuNPs were characterized by TEM (JEM-2100, JEOL, Japan) and average particle size as well as particle size distribution were calculated by measuring particles manually from the TEM images (see the Supporting Information, Figure S1).

Preparation of Polyelectrolyte Multilayer on PDMS Stamp. The multilayer assembly method on the PDMS stamp was adapted from a previous work.[22] Briefly, the stamp was dipped in 50 mM PAH solution (pH: 10.5) for 10 min. After the stamp was rinsed with DI water vigorously, PSS (10 mM, 0.1 M NaCl) and PDAC (20 mM, 0.1 M NaCl) were alternatively deposited on the stamp via spin coating at 3000 rpm for 5 s. The process was repeated until obtaining the $(PAH)_1(PSS/PDAC)_{10}$ multilayer system. After each polyelectrolyte coating, the stamp was rinsed twice with DI water via spinning with the aforementioned condition. Finally, the stamp was dried under N_2 gas flow. As a consequence, the stamp has positively charged PDAC at the outermost layer.

Multilayer Transfer Printing. Both the cleaned Si wafer substrate and the polyelectrolyte coated PDMS stamp was subjected to the vapor of boiling water for 1 min to enhance the electrostatic interaction between the substrate and the stamp. Immediately after exposing to humidity, the stamp was slightly pressed on the substrate and allowed to wait for 30 min. When the stamp was released, the patterns of polyelectrolyte multilayer film on the substrate were successfully obtained. Finally, the substrate was rinsed with DI water several times to remove the unbounded polyelectrolytes.

Fabrication of Gold Patterns. The top surface of the transfer printed multilayer is expected to be the positively charged PAH layer as reported previously.[21,22] Immediately after multilayer transfer printing and rinsing, the substrate was dipped in negatively charged AuNP solution for 15, 30, 45, 60, and 120 min. The pH of the AuNP solution was measured as 5.5, which is well below the pK_a of PAH (8.8). Thus, AuNPs were selectively deposited on the PAH layer. Next, the substrate was immersed in freshly prepared electroless plating solution (0.3 mM $HAuCl_4$ and 0.4 mM NH_2OH) under shaking at 120 rpm for 3, 5, 7, and 10 min for the formation of continuous gold patterns.[27] Here, the AuNPs were utilized as seeds for electroless plating of gold on the polyelectrolyte pattern.

Characterizations. The patterned substrates were analyzed by optical microscope (BX51, Olympus, Japan), AFM (XE-70, Park Systems, Korea) and FE-SEM equipped with EDX (S-4700, Hitachi High-Tech, Japan). Electrical conductivity was measured via four-point probe method by Hall Effect measurement system (7707A, Lake Shore Cryotronics Inc., USA). Optical properties of the AuNP monolayer were investigated with UV−vis spectrometer (Lambda 750, Perkin-Elmer, USA).

RESULTS AND DISCUSSION

Multilayer transfer printing. The schematic diagram for the multilayer transfer printing is illustrated in Figure 1A. The principle of the multilayer transfer printing depends on two factors; (1) The outermost layer of the multilayer coated stamp and the substrate should be oppositely charged, and (2) the adhesion force of the multilayer coated on the stamp should be in the favor of the substrate rather than the stamp. Thus, in this work, the PDMS stamp was coated with $(PAH)_1/(PSS/PDAC)_{10}$ multilayer system in order to ensure good adhesion

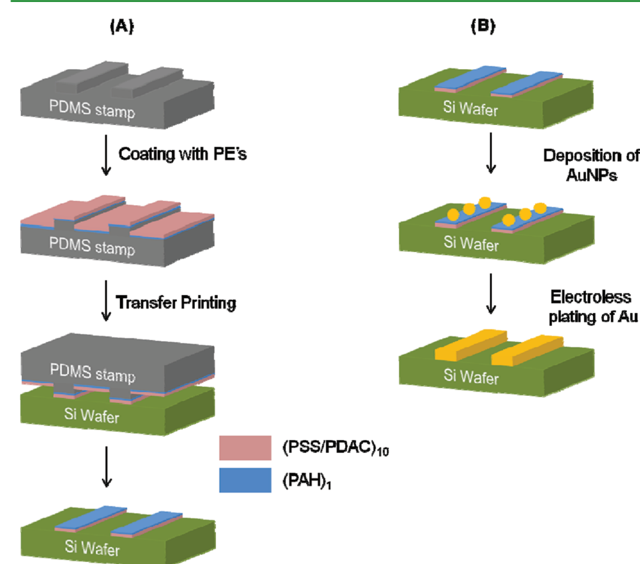

Figure 1. Schematic illustration of (A) multilayer transfer printing and (B) gold pattern fabrication.

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and highly selective patterning. The PSS (negatively charged) and PDAC (positively charged) are strong polyelectrolytes so they have strong electrostatic interaction to each other. In addition, the PDAC at the top layer of the stamp can bind strongly to the negatively charged Si substrate. The critical issue is the deposition of the PAH layer on the stamp via hydrophobic interaction which acts as a weak boundary layer between the PDMS and the $(PSS/PDAC)_{10}$ system, and thus facilitates the successful multilayer transfer printing. Although it is a positively charged polymer, printing of only PAH layer is not possible due to the decreased charged along the backbone of PAH as well as the printing requires highly charged substrate and multilayer on the PDMS stamp.

First, we have investigated the transferred $(PAH)_1/(PSS/PDAC)_n$ multilayer system (n = 2,4,6,8,10) with AFM and optical microscope. However, we have found that $(PAH)_1/(PSS/PDAC)_{10}$ is the optimum multilayer system in terms of reproducibility and uniformity. We have yet to clearly understand the reasons for the optimum multilayer system, which needs detailed morphological and chemical analysis, and is beyond the scope of this work. Successful transfer of the $(PAH)_1/(PSS/PDAC)_{10}$ to the Si wafer substrate is evidenced by the optical microscope and AFM as demonstrated in panels A and B in Figure 2, respectively. It is shown that very clean and selective multilayer patterns with 10 μm features were successfully obtained. In contrast to low MW silane molecules, lateral diffusion of the polymers were not observed, resulting in clean and precise patterns. This can be attributed to the high MW of polyelectrolytes and the strong ionic interaction of the polyelectrolytes to each other and to the substrate. The thickness of the $(PAH)_1(PSS/PDAC)_{10}$ was measured as ~35 nm (Figure 2-C), which in consistent with the previous work.[21] In addition, it was observed that the thickness of the transferred layer increases linearly with the number of layers and the thickness of $(PAH)_1$ and $(PSS/PDAC)_1$ layers were found as 5 and 1.5 nm, respectively (not shown here).

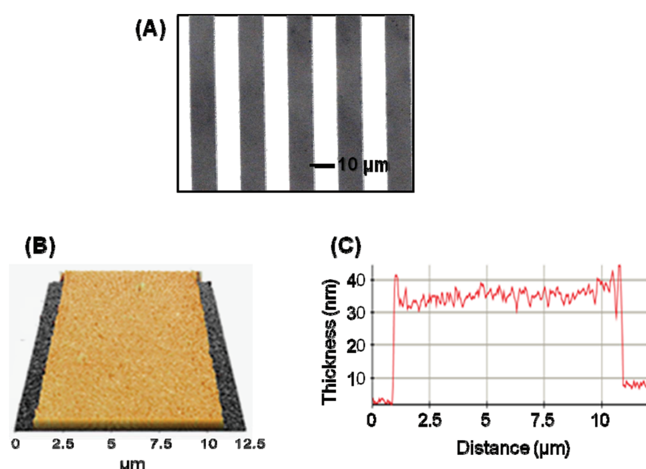


Figure 2. (A) Optical microscope image, (B) AFM image, and (C) thickness profile of the transfer printed $(PAH)_1(PSS/PDAC)_{10}$ multilayer system.

Fabrication of Gold Patterns. The schematic diagram for the preparation of the gold patterns is demonstrated in Figure 1B. The multilayer transfer printed substrate was dipped in AuNP solution, followed by immersing in electroless plating solution. The mechanism relies on deposition of negatively charged AuNPs selectively on the positively charged PAH layer via ionic interaction. The PAH layer (pK_a = 8.8) is fully ionized in AuNP solution (pH 5.5) and thus AuNP adsorption was possible. Then, these AuNPs act as the seeds for the electroless plating of gold.

First, the effect of dipping time in AuNP solution was investigated via UV–vis and FE-SEM analysis. Glass substrate and flat PDMS stamp was used for these experiments. Figure 3-A shows the UV–vis spectra of AuNP monolayer with different dipping time of the substrate. The strong absorption peak appeared at 540 nm could be attributed to the surface plasmon resonance of discrete AuNPs.[28] However, the absorption peak shifted to longer wavelength (red shift) compared to absorption of AuNP solution at 518 nm. This may be explained by the strong electromagnetic coupling of the nanoparticles that come into close proximity, which led to a shift to lower energy modes.[29] As demonstrated in Figure 3B, the intensity of this peak is observed to increase with time and no considerable change is observed for the dipping time more than 60 min. The surface coverage of the AuNPs on the substrate as a function of dipping time displays the same trend with the UV–vis absorbance and reaches to ~40% for 60 min dipping (Figure 4A). The surface coverage is higher than 30% obtained by the $PEI/[(PSS/PAH)_3AuNP]_1$ multilayer system in a previous report,[30] which can be explained by the high salt concentration of polyelectrolyte solutions (1 M NaCl), resulted in thick and rough multilayer film with less ionic groups due to shielding effect of salt. On the other hand, the surface coverage is lower than the theoretical jamming limit (~55%)[31] determined by the

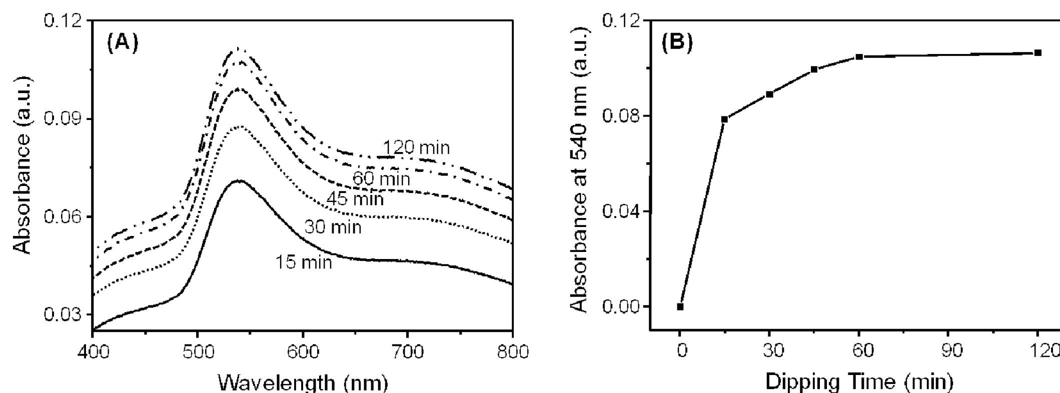


Figure 3. (A) UV–vis spectra and (B) absorbance at 540 nm of AuNP monolayer as a function of dipping time.

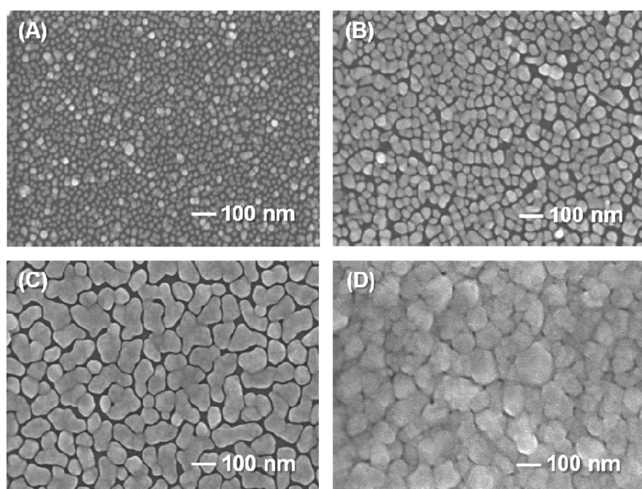


Figure 4. FE-SEM micrographs of (A) AuNP monolayer and gold layer deposited on AuNP monolayer via electroless plating for (B) 3, (C) 7, and (D) 10 min.

random sequential adsorption of noninteracting solid spheres, which can be explained by the ionic repulsion between the citrate stabilized AuNPs in the solution.[26]

Then, the electroless plating of gold on the AuNP deposited substrate was carried out. Figure 4 shows the Au^{3+}/NH_2OH seeding on the AuNP monolayer as a function of time. It is clear that plating for 3 min leads to an enlargement in both particle height and width (Figure 4B) with discontinuties between the particles. Increasing the plating time to 7 min results in large gold aggregates, which can be attributed to the fusion of enlarged particles (Figure 4C). However, discontinuties are still present between the aggregates. After 10 min plating, the morphology of the gold layer is indistinguishable from the granular metal films obtained by thermal evaporation (Figure 4D).[32] It is notable that the isolated enlarged gold aggregates past the percolation threshold to form conducting metal structures. Subsequently, the rms roughness of this sample (Figure 4D) was measured and found as 3.5 nm, which is slightly higher than the value of metal films prepared by evaporation at high vacuum.[33] Furthermore, formation of gold layer on the substrate was evidenced by EDX analysis as demonstrated in Figure 5A. On the other hand, presence of carbon and oxygen peaks could be explained by the presence of polyelectrolytes under the gold layer. Then, the electrical characterization of the gold layer was performed as displayed in Figure 5B. The *I*−*V* curve shows ohmic behavior, indicating the formation of continuous metallic gold layer, which is consistent with the FE-SEM micrograph (Figure 4-D). The electrical conductivity was calculated as $2.5 \times 10^5\ \Omega^{-1}\ cm^{-1}$, which is higher than the previous works.[8,9,12,19,34] However, it is worthy to note that the conductivity is still lower than the value of bulk gold ($4 \times 10^5\ \Omega^{-1}\ cm^{-1}$), which could be attributed to the grain boundaries and defects,[18,35] as well as enhanced carrier scattering due to polycrystalline nature and high rms roughness of gold layer as reported previously.[9]

Finally, gold patterns were prepared by multilayer transfer printing of polyelectrolytes with patterned stamp, followed by AuNP deposition for 60 min and then electroless plating for 10 min. The results showed nice and clean gold patterns with 10 μm line width, as shown in Figure 6A. Compared to Figure 2A, the pattern color changed from black to shiny gold upon electroless plating. Clean patterns without Au on the unpatterned areas can be attributed to the successful transfer of the polyelectrolytes with the PDMS stamp and subsequent deposition of AuNPs. In addition, FE-SEM micrographs also confirmed the formation of continuous metallic gold patterns (Figure 6B). However, the edge of the pattern are not smooth, which can be explained by the lateral enlargement of the gold nanoparticles via electroless plating. The thickness of the patterned layer was measured as ~95 nm (Figure 6C), indicating the deposition of ~60 nm gold layer on the polyelectrolyte layer (~35 nm) consistent with the previous work.[19] It is worth noting that the smallest feature that can be obtained with our approach is 1 μm, because of the low elastic

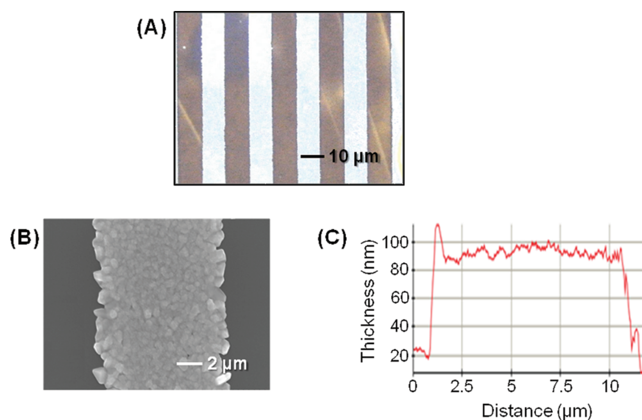
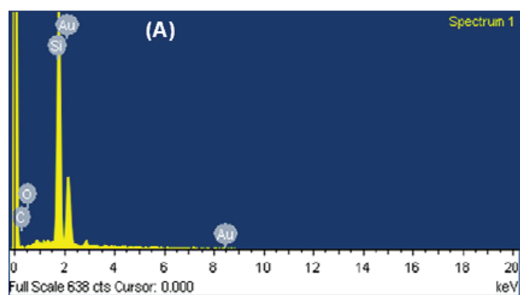


Figure 6. (A) Optical microscope image, (B) high-magnification FE-SEM micrograph, and (C) thickness profile of gold pattern.



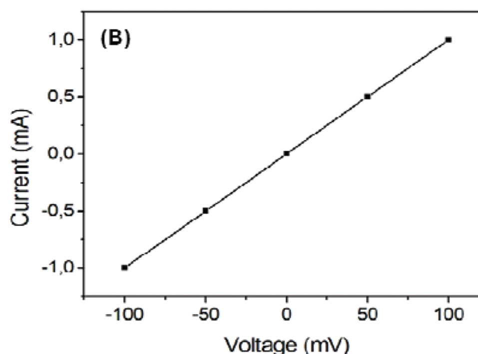


Figure 5. (A) EDX analysis and (B) electrical characterization of gold layer obtained via electroless plating for 10 min.

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modulus of PDMS, which causes the stamp to deform, buckle, or collapse.

In this work, we demonstrated a facile and low-cost three-step method (multilayer transfer printing + AuNP seeding + electroless plating) for fabrication of gold patterns on Si wafer substrate. The advantage of the proposed approach over a one-step process (masking + evaporation of metal) is that it could be reproduced easily with commercial chemicals and polymers in a simple lab environment without any need for expensive and sophisticated equipments. Besides, copper plating without seed (two-step process) was achieved on the self-assembled monolayer (SAM) of 4-mercaptobenzoic acid and 16-mercaptohexadecanoic acid, because of the reaction between −COOH moieties and copper ion.[36−38] However, this approach is only limited for gold and copper as substrate and electroless plating metal, respectively, when compared to our approach.

On the other hand, our approach can be easily adapted for preparation of various metals, including Cu and Ag on Si wafer as well as different polymer substrates. We believe that it may be a suitable technique for fabrication of metal electrodes and interconnects for flexible electronics. However, one may think that adhesion and the crack of the pattern could a be problem while fabricating metal patterns on flexible polymer substrates. Surface modification of the polymer substrate via plasma etching will solve the adhesion of the patterns to the substrate as shown previously.[21,34] Meanwhile, we believe that highly flexible substrate, including PI and PET as well as printed polyelectrolyte multilayer, will inhibit the crack formation of the metal pattern. In addition, crack formation was not reported in the previous works by Park[10] and Huang,[12] who prepared gold patterns on flexible PI and PET substrate, respectively.

CONCLUSIONS

Gold patterns were fabricated on Si wafer substrate by multilayer transfer printing of polyelectrolytes, followed by selective AuNP deposition and then electroless plating of gold. Major findings are summarized as follows;

(1) Multilayer transfer printing of $(PAH)_1(PSS/PDAC)_{10}$ on Si wafer substrate provided nice and clean polymer patterns with positively charged PAH at the outermost layer.
(2) Optimum dipping time in AuNP solution was found as 60 min, which led to surface coverage of 40%.
(3) Electroless plating for 10 min resulted in gold layer indistinguishable from the granular metal films with electrical conductivity of $2.5 \times 10^5\ \Omega^{-1}\ cm^{-1}$.
(4) Shiny gold patterns were prepared with 10 μm features without any formation of gold on unstamped area.

ASSOCIATED CONTENT

Supporting Information

TEM image and size distribution graph of AuNPs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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