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A rapid technique for the direct metallization of PDMS substrates for flexible and stretchable electronics applications

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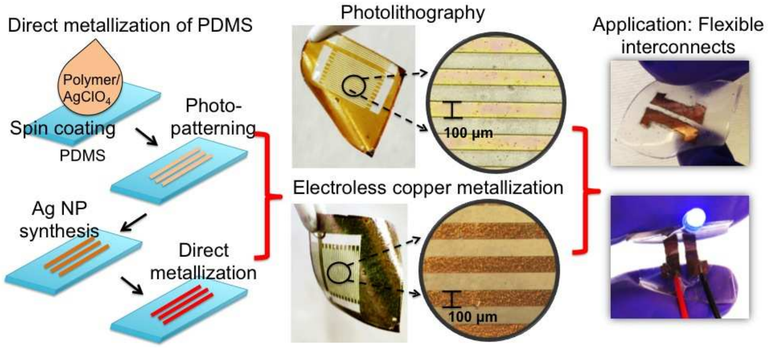
Highlights

- Crack-free deposition of electroless copper over elastomeric surfaces;
- Strong metal-to-PDMS surface adhesion;
- Copper film remains conductive whilst it undergoes bending and stretching deformations;
- Copper-plated PDMS substrates have high flexibility (up to 180°).

Abstract

Metallization of a polydimethylsiloxane (PDMS)-based substrate is a challenge due to the difficulties in forming crack-free polymer and metal features using standard deposition techniques. Frequently, additional adhesion layers, rigid substrates, multiple processing steps (lift-off and etching) and expensive metal sputtering techniques are required, to achieve such metal patterns. This work presents a novel and rapid technique for the direct metallization of PDMS substrates using photolithography and electroless copper plating. The method has the advantage of not requiring expensive vacuum processing or multiple metallization steps. Electroless copper layer is demonstrated to have a strong adhesion to PDMS substrate with a high conductivity of $(3.6 \pm 0.7) \times 10^7$ S/m, which is close to the bulk copper (5.9×10^7 S/m). The copper-plated PDMS substrate displays mechanical and electrical stability whilst undergoing stretching deformations up to 10% due to applied strain. A functional electronic circuit was fabricated as a demonstration of the mechanical integrity of the copper-plated PDMS after bending.

Graphical abstract



Keywords: copper-plated PDMS, direct metallization, electroless plating, flexible electronics, stretchable electronics

1. Introduction

Stretchable and flexible electronics have received great interest for multiple applications ranging from wearable electronics, soft robotics, displays to bioelectronics [1], [2]. The increasing demand for flexible microelectronic systems requires the development of flexible circuits with interconnections that can withstand mechanical stresses under high strains [3]. Various nanocomposite materials and elastic polymers such as polyimide, polyethylene naphthalate and polyethylene terephthalate are currently being investigated as soft substrates for fabrication of flexible electronic devices with stretchable interconnections linking electronic parts [4].

PDMS elastomer is an excellent candidate for flexible electronics due to its stretchable and bending characteristics [5]. However, the integration of circuitry is a challenge due to the difficulty encountered in directly depositing a conductive material. Frequently, cracks are formed in the photoresist during photolithography and in the metal during the sputtering processes [6]. Moreover, adhesion is poor and additional adhesion layers, bonding agents and multiple processing steps (lift-off and etching), are required to achieve a crack-free photoresist and metal patterning on PDMS [7]. Expensive vacuum techniques such as e-beam evaporation or sputtering are used for metal deposition on PDMS-based substrates. Direct metal transfer technology is another example of metal deposition onto polymer substrates. However, this method usually requires an additional rigid substrate (e.g. glass and silicon wafer) to prepare metal patterns prior to their transfer onto PDMS substrates [8]. An economic and simple technique is therefore needed to provide a high metal-to-PDMS surface adhesion that remains conductive whilst the substrate undergoes bending and stretching deformations. The formation of conductive features by direct metallization triggered by light patterning addresses these issues [9].

In this work, we have developed a rapid technique for the direct metallization of PDMS substrates by reliable photolithography and electroless copper plating methods. Fig. 1 shows the newly developed photo-patterning and metallization steps. Modified DNQ-novolac photoresist polymer (hereafter - polymer) was mixed with $AgClO_4$ salt, which was thermally reduced to Ag nanoparticles (NPs) inside the polymer during a hard bake step [4]. Crack-free metal patterns are achieved through optimization of photolithography parameters. Analysis of cracking and buckling formations in polymer and metal films related to under-optimized and non-optimized fabrication parameters has been performed, through the study of the optical micrographs. The electromechanical behaviour of metal patterns on PDMS was investigated by measuring changes in electrical conductivity in response to strain and bending cycling deformations, As a proof of concept, we demonstrate a flexible light emitting diode (LED) circuit fabricated by the developed metallization method and show the circuit working during the bending test.

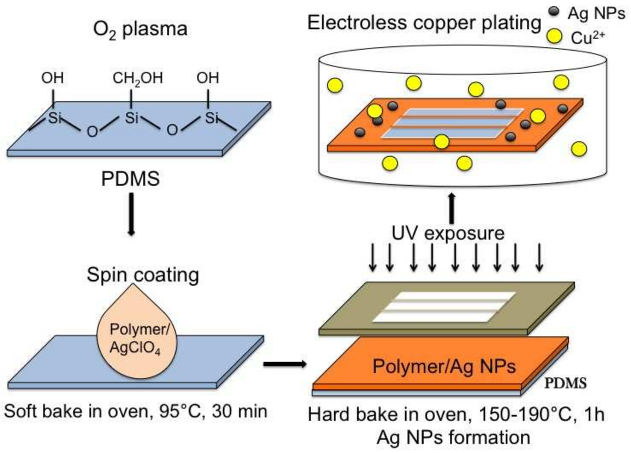


Fig 1. Schematic steps of the direct metallization of PDMS substrate using photolithography and electroless copper plating.

2. Experimental

Two types of PDMS were tested: commercial PDMS-based gel sheets supplied by Gel-Pak® (150 μm thickness), and laboratory-prepared PDMS substrates prepared by curing a silicone elastomer (Sylgard® 184) with a curing agent (Sylgard® 184) in a 10:1 ratio in a convection oven (Binder, Germany). PDMS substrates were treated with oxygen plasma prior to polymer/$AgClO_4$ spin coating to increase PDMS surface roughness. Oxygen plasma was applied using the PLASMALAB device (Oxford Instruments Plasma Technology) for 10 s at 100 mTorr pressure with an oxygen plasma dose of 1.5 kJ (plasma power, 150 W × time, 10 s).

2.1 Synthesis of Ag NPs seeds inside the polymer and photo-patterning method

0.1 M silver perchlorate ($AgClO_4$, Sigma Aldrich, 97 %) concentration was received by dissolving it in 1-methoxy 2-propylacetate (MPA) (Sigma Aldrich, 99%). Ma-P 1215 photoresist (MicroResist Technology) was mixed with silver solution in 1:1 ratio. The resultant mixture was spin coated on PDMS substrates at 3000 rpm for 30 s and soft baked at 95°C for 30 minutes in an oven. PDMS substrates were exposed to UV light at 14 $mWcm^{-2}$ using a Karl Suss MJB 3 UV mask aligner and developed with AZ 326 developer. The samples were hard baked in a convection oven using ramping temperature profile for 1 hour.

2.2 Fabrication of electroless copper films and interconnections

Electroless copper bath solution was prepared by dissolving 6 g of copper sulfate (98%, Sigma Aldrich), 8 g of sodium hydroxide (98.5%, Acros Organics), and 28 g of potassium tartrate (99%, Fisher Scientific) into 200 ml of DI water. Before electroless plating, the concentrated solution was diluted with DI water in the ratio of 1:1 and 2 ml of formaldehyde (37 %, Acros Organics) was added. Ma-P 1200 series photoresists have an outstanding stability in acid and alkaline plating baths, therefore, treated substrates were immersed into electroless copper bath for 10 minutes. Electroless copper plating was carried out at 30°C.

Flexible LED circuit was fabricated as a proof of concept. Conductive electroless copper interconnections were fabricated on 1 mm thick PDMS, using a laboratory-made photo-mask and its bending properties were tested. Flexible LED circuit consists of a 3 mm LED with a 3 V battery that were connected to the flexible interconnections.

2.3 Characterization and measurement

Copper film thickness and PDMS surface roughness were measured by a Dektak^3 Stylus optical profilometer and optical images of the film surface were obtained using LEICA CTR 6500 instrument. All resistance measurements were performed by a two-point probe technique using SIGNATONE S-1160 probe station. The metal plating quality was tested using the IPC -TM-650 scotch tape test [10]. Pressure sensitive tape Type 1, Class B was firmly applied to metal surface removing all air entrapment. The test was performed three times with fresh tape used for each test. The tapes were visually examined for presence of any portion of the film having been removed from the PDMS surface.

Copper-plated PDMS substrates were stretched with a laboratory-made mechanical strain machine that consists of a displacement-sliding table and clamps to hold a film. Mechanical strain machine is capable to apply up to 80% uniaxial strain to metallized patterns. Bending cycles experiments of 10,000 cycles were conducted on a Dynamic Mechanical Analyzer (DMA, TA Instruments, Model Q800) in single cantilever mode with amplitudes of 2.5 mm and 5.0 mm at a frequency of 1Hz at room temperature. Tested PDMS substrates with copper film have 17.1 mm length, 10.4 mm width and 1.2 mm thickness.

3. Results and discussion

The PDMS surface roughness is affected by applied oxygen plasma [11]. Therefore, the surface roughness of PDMS-based Gel-Pak® films increased from 10 ± 2 nm to 53 ± 4 nm after oxygen plasma treatment. As for laboratory-prepared PDMS, the surface roughness increased from 7 ± 2 nm to 33 ± 8 nm. The increase of the surface roughness allows for uniform coating of the PDMS surface with polymer/$AgClO_4$ solution. The formation and growth of Ag NPs inside the polymer matrix occurs by thermal induced reduction of Ag(I) to Ag(0) at high temperatures [12]. The Ag NPs act as seeding catalysts for copper ions adsorption during the electroless copper metallization step [13]. Electroless copper plating for 10 minutes resulted in copper thickness of 0.44 ± 0.05 µm. Deposition of the metal film over the elastomeric surface may result however in the formation of cracks and buckles. For this reason, we discuss in the following sections film morphology and study the electromechanical behaviour of the copper film on PDMS surface by applying strain and bending deformations.

3.1 Morphology analysis of polymer/Ag NPs and metal film on PDMS

Process-induced cracks in spin coated polymer/$AgClO_4$ film on PDMS occurs during the lithographic patterning processes such as the soft and hard baking steps. These cracks arise from the expansion of the elastomer surface due to applied temperatures, which induces a thermal tensile stress over the polymer/$AgClO_4$ film. This leads to the polymer/$AgClO_4$ film rupturing and may also cause the underlying PDMS substrate to fracture [14]. Fig. 2a shows the process induced cracks in PDMS when films experience sudden temperature change due to heating and cooling. Developed fractures in PDMS during the soft and hard baking steps further effect the quality of polymer/$AgClO_4$ and metal patterns on the PDMS surface (Fig. 2b). The existing fractures in PDMS and polymer/Ag NPs extend into a copper layer and introduce metal cracks. Therefore, it is important to avoid pre-existing cracks in

PDMS and polymer/Ag NPs prior to metallization. Careful control of the baking temperature allows crack elimination. Fractures were avoided during soft and hard baking processes by utilizing homogenous heating and cooling in an oven by applying temperature ramping of 5°C/min.

Compressive stress can also build up during the cooling process which results in buckling or wrinkle formations [14]. The temperature chosen during the hard baking step is to promote thermal reduction of Ag(I) to Ag NPs. At 190°C, buckles were developed (Fig. 2 c-d), however, decreasing the temperature down to 150°C reduced buckling formation. Fig. 3 shows received crack-free polymer/Ag NPs patterns which lead to crack-free copper metal patterns on PDMS surface.

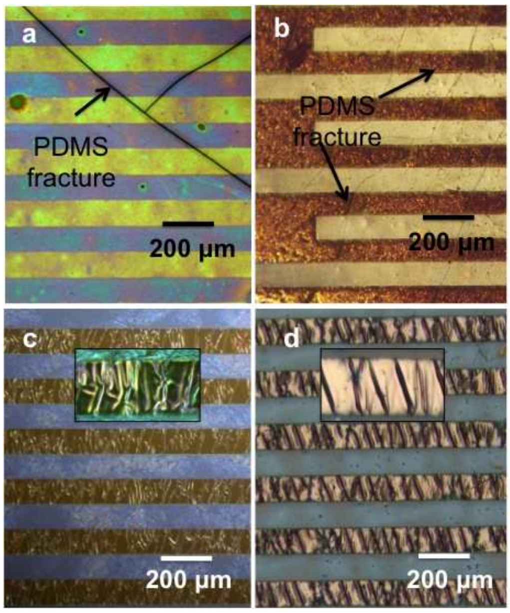


Fig. 2. Study of optical micrographs for PDMS fractures due to sudden baking temperature changes (a) polymer/Ag NPs patterns and (b) copper metal patterns. Buckle formations due to 190°C hard baking temperature (c) polymer/Ag NPs patterns and (d) copper metal patterns.

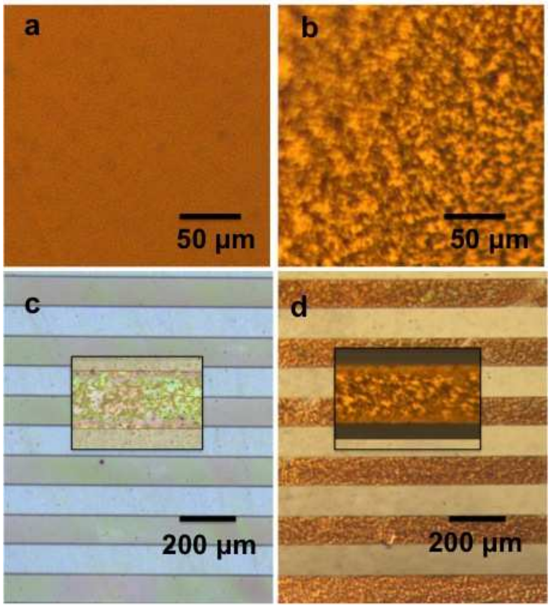


Fig. 3. Study of optical micrographs: (a) polymer/Ag NPs film baked at 150°C, (b) copper metal film, (c) polymer/Ag NPs pattern baked at 150°C, (d) copper metal pattern.

3.2 Mechanical and electrical properties

The formation of strong adhesion between the copper layer and PDMS is important for mechanical and electrical stability. The fabricated copper film on PDMS substrate has a strong adhesion and passes the scotch-tape tests. The mechanical properties of copper micropatterns on PDMS substrate is further tested with application of the uniaxial longitudinal strain parallel to the direction of the copper micro-lines. Fig. 4 shows a development of strain-induced cracking in copper patterns on PDMS substrate as a function of the applied uniaxial strain. At zero strain, no process-induced cracks are observed. The strain-induced cracks start forming at 10% applied strain. As the applied strain increases, the density of cracks increases (Fig. 4g). The increase of the applied strain results in an enlarged crack width. The arrows in Fig. 4 (d-e) show the visual comparison between the crack widths due to the increase of the consecutive applied strain.

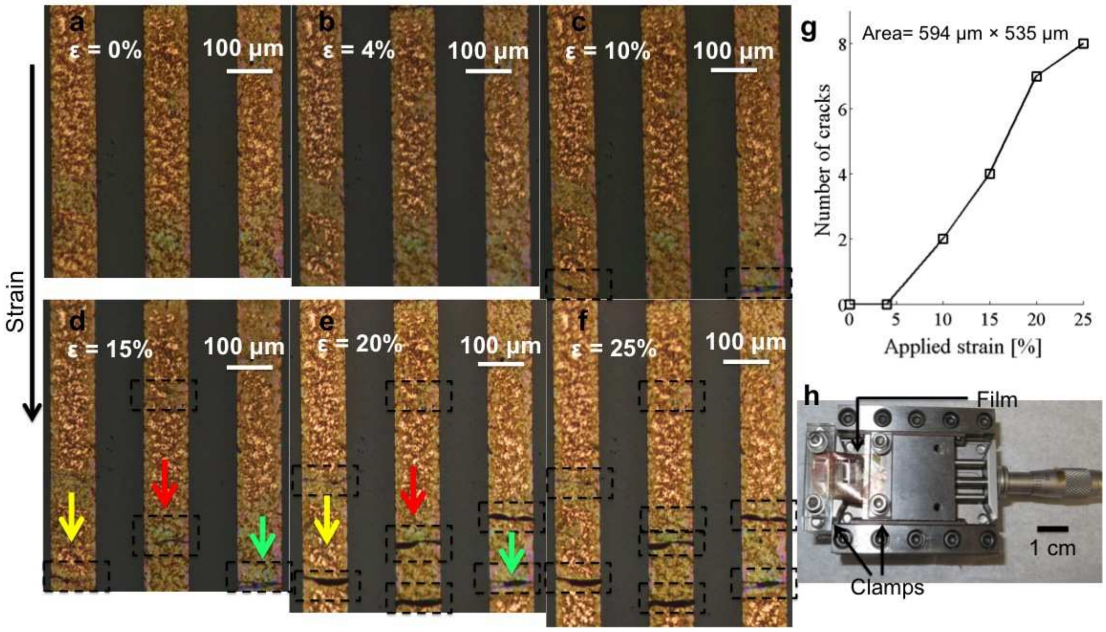


Fig. 4. Development of the strain-induced cracks in copper micropattern due to applied uniaxial strain. Strain is applied parallel to the copper line patterns. From (a) to (f) the applied strain varies from 0% to 25%. (g) Density of strain-induced cracks as a function of the applied strain. (h) laboratory-made mechanical strain machine.

Fig. 5a shows the electromechanical behaviour of the copper film as a function of the applied strain. At zero strain, the conductivity of the copper film is (3.6 ± 0.7) $\times 10^7$ S/m. The conductivity drops to (2.5 ± 1.3) $\times 10^7$ S/m at 10% strain. The longitudinal applied strain leads to the formation of horizontal micro-cracks in the copper film. Therefore, formed micro-cracks contribute to a reduction in the electrical conductivity. Further increase in the strain leads to a more discontinuous copper film with a conductivity approaching (0.5 ± 0.5) $\times 10^7$ S/m at 15% applied strain. To further study the electromechanical behaviour of the copper film on the PDMS substrate, mechanical cycling tests were performed. Fig. 5b shows a change in normalized resistance (R/R_0) as a function of the bending cycles. Copper films were bended to 2.5 and 5.0 mm amplitudes. The resistance increased by almost 1.4 times when copper film was bended for 1,000 cycles for both bending amplitudes. As the bending proceeded, the change in resistance increased and the conductivity dropped by a factor of two when copper film was bended to 2.5 mm amplitude and a factor of 4.5 when copper film was bended to 5.0 mm amplitude, after 10,000 cycles.

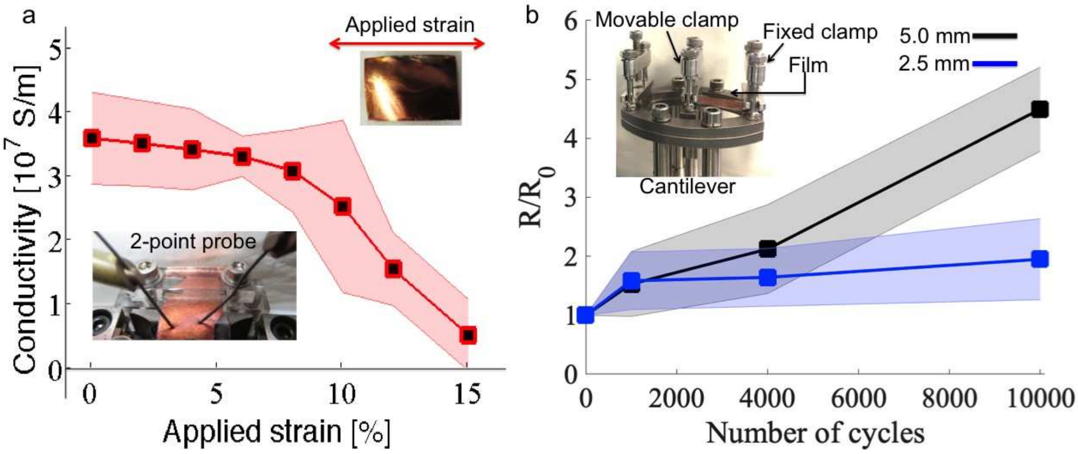


Fig.5. Dynamic electromechanical analysis of the copper-plated PDMS films. (a) Change in conductivity as a function of the applied strain. The insets show a copper film with the direction of the applied strain and a set up for resistance measurement with two-point probe. (b) Change in resistance during 10,000 cycling test for 2.5 mm and 5 mm amplitudes. The inset shows a cantilever with the movable and fixed clamps with a clamped film.

3.3 Application. Interconnections and flexible electronic circuit

Copper-plated PDMS was tested as a flexible LED circuit. Fig. 6a shows electroless copper interconnections fabricated on 1 mm thick PDMS substrate. An LED and battery were attached to the interconnections to form an electronic circuit (Fig.6b). With the battery on, we observed the LED to light up. A static bending test was further performed to study the electrical properties of the electroless copper interconnects on the PDMS surface (Fig.6 c-f). The electroless copper interconnections are located on the compressive side of the curvature. Normal LED operating mode was observed while the circuit was bent to 45°, 90°, 135° and 180°. During the static bending, interconnections remained conductive and LED remained switched on up to 180° bending angle.

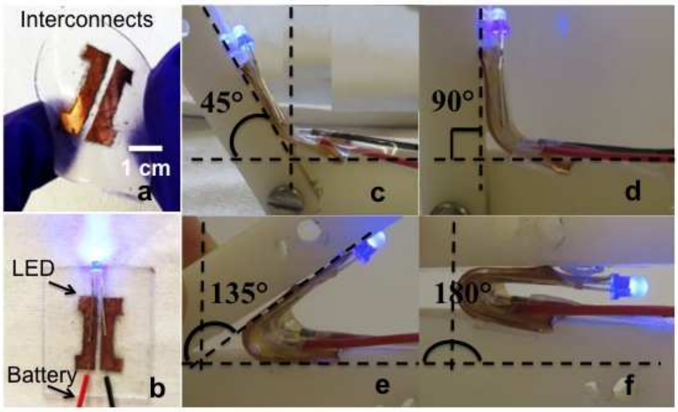


Fig. 6. Application of the PDMS metallized with copper composite. (a) Interconnections, (b) LED electronic circuit, (c-f) static bending tests of the flexible LED circuit.

4. Conclusions

We have developed a direct, selective and rapid metallization method of PDMS elastomers. Formed copper films and micro-patterns have advantages of high conductivity and good adhesion to PDMS substrate. Optimization of photolithographic parameters reduced process-induced cracks and buckles in polymer/$AgClO_4$ and subsequently in copper layer. The applied uniaxial strain resulted in crack-free copper film up to 10% strain. The conductivity shows good stability up to 10% applied strain, after which conductivity dropped 1.4 times compared to the initial measurement. Flexible LED circuit demonstrated that copper-plated PDMS has a high flexibility (up to 180°). The proposed low-cost and rapid metallization method of PDMS substrates is a promising fabrication technique, which is compatible with standard microfabrication processes, for use in flexible and stretchable electronics applications.

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