

Three dimensional metal pattern transfer for replica molded microstructures

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We report a replica molding process for simultaneously forming a three dimensional metal pattern on the surface of molded polymer microstructures. This technique uses noncovalent surface forces to guide the transfer of thin metal films from the three dimensional features of high aspect ratio poly(dimethylsiloxane) micromolds to polymeric replicates. The utility of this technique has been demonstrated by the fabrication of organic coplanar waveguides integrated with vertical *Ka*-band monopole antenna radiators. These microwave systems show good performance with over 18% bandwidth and greater than 16 dB return loss, demonstrating the versatility of this process. © 2009 American Institute of Physics. [DOI: 10.1063/1.3063122]

Fabrication of three dimensional (3D) metallic micro structures on a large scale at low cost has many applications in microelectronics, wireless communications, and biofluidics.¹⁻³ Previously, such structures have been fabricated by first forming polymeric microstructures and subsequently coating them with metal. Polymeric microstructures can be easily replicated by molding, which is one of the most widely used soft lithography techniques. However, it remains a challenge to selectively coat these molded polymer structures with metal when specific patterns of metal are required; this problem is exacerbated when the molded structure has sufficient three dimensionality such that planar lithography processing of the metal cannot be used. Nanotransfer printing (nTP), a metal patterning technique compatible with soft lithography, uses a metal-coated, patterned polydimethylsiloxane (PDMS) stamp to transfer a metal film onto various substrates. Transferred metal structures with dimensions as small as a few hundred nanometers and an edge roughness as small as a few nanometers have been demonstrated.⁴⁻⁶ The nTP technique has been exploited in the applications of organic microelectronics.^{7,8} However, metal pattern transfer based on nTP has been demonstrated only on relatively planar substrates and has been limited to two dimensional (2D) patterns. We report a 3D metal pattern transferring technique which is integral with the molding process. An inverse transfer printing has been exploited for metal patterning on the mold surface, followed by polymer casting and separation, resulting in prepatterned 3D metal transfer to the casting material. Several polymers commonly used in micromolding processes have been utilized for 3D metal transfer demonstration. Control of polymer surface energy allows successful transfer. We observe that the surface roughness in 3D metal transfer is not as critical as in the 2D nTP process. We illustrate this technique by successfully fabricating organic radio frequency (rf) radiator circuits.

Figure 1 schematically illustrates the fabrication steps of the 3D metal pattern transfer process. A PDMS stamp is created by casting and curing Sylgard 184 prepolymer

against a master patterned by conventional photolithography and etching. Then the PDMS stamp is coated with a thin metal film (from 50 to 100 nm Au or Au/Ti, and Ti is from

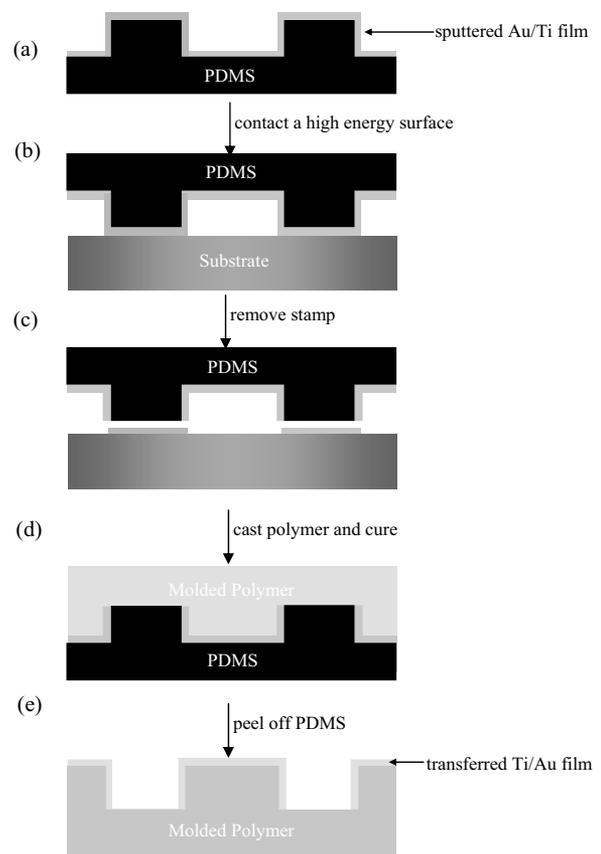


FIG. 1. A schematic representation outlining each step of the procedure of 3D metal pattern transfer process. (a) A PDMS stamp, which is fabricated by soft lithography, is coated with a thin metal film of Au or Au/Ti. (b) The PDMS stamp is contacted at room temperature against a high energy surface such as silicon substrate spin coated with PU. (c) After PU is cured, the stamp mold is peeled off and the metal pattern on the raised features of the stamp is bound to the substrate. (d) Polymers (in liquid state) are cast into the PDMS stamp mold in vacuum until full wetting. (e) After the polymers are cured and cooled down, the PDMS stamp mold is peeled off and the metal film is completely transferred to the cast polymers.

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10 to 30 nm as a seed layer for the transferred Au) which covers not only the raised and recessed regions of the stamp mold but also the sidewalls [Fig. 1(a)]. A transfer printing process is performed to remove the metal film on the raised regions of the stamp mold. In this process immediately placing the freshly metal-coated stamp mold onto a flat, smooth substrate of relatively high surface energy compared with PDMS leads to “wetting” that provides intimate contact between the two surfaces [Fig. 1(b)]. The substrate that we typically use is a silicon wafer spin coated with UV curable polyurethane (PU). After the PU is cured, the stamp mold is gently peeled off and the metal layer on the raised region is printed to the PU coated silicon wafer [Fig. 1(c)]. However, our interest is the original PDMS stamp with metal film coated on the recessed region. An appropriate structural polymer in a liquid state (e.g., uncured, melted, or solvent) is cast into the PDMS stamp mold. Vacuum and heat may be utilized to ensure that the liquid-state polymer fully wets the recessed regions of the stamp mold [Fig. 1(d)]. After the cast polymer is solidified, the PDMS stamp mold is peeled off and the metal film within the recessed region is completely transferred to the molded structures [Fig. 1(e)].

Figures 2(a) and 2(b) display a set of microscope and scanning electron microscopy (SEM) images of several types of 3D structures with some representative scale features made of various polymers. The dimensions range from 2 to 100 μm , and the aspect ratio defined as width to height is approximately 1:1. The extruded 3D structures are coated by transferred metal film while there is no metal observed on the bottom substrate due to the pre patterning by transfer printing. By using this 3D metal transferring process, not only extruded microstructures such as posts or lines can be metallized during replica molding, but also a patterned electrical connection of these structures can be formed at the same time. Figure 2(c) shows a molded micropost array coated with gold film by metal transfer, and the posts are electrically interconnected so as to form a “checkerboard” pattern. The mold masters are fabricated by gray scale lithography of SU-8 to form a two level structure.⁹ The lines in the bottom define the electrical pattern and the posts are in the top level. By removing the metal on the raised area of the PDMS stamp, the metal film is patterned and transferred to the molded SLA structures.

Similar to conventional nTP operating by exploitation of noncovalent surface forces,⁸ the metal transfer mechanism here is also based on differing strengths of nonspecific adhesion between the PDMS-metal and polymer-metal interfaces. For most materials, the adhesion strength of the PDMS interface is weaker than that of the metal/cast polymer interface due primarily to the extremely low surface energy (19.8 mJ/m^2) of the PDMS. Several polymers that are widely used in replica molding have been utilized for 3D metal transfer demonstration: thermoplastic polymers such as polymethyl methacrylate (PMMA), PU; biodegradable polymers such as poly(L-lactic acid); photocurable polymers such as epoxy-acrylate resin; and negative photo resists such as SU-8. For these materials, the metal film is completely transferred and the transferred gold film on the molded polymers shows similar adhesion strength with the directly deposited gold film based on Scotch™ tape adhesion tests. It has been reported in nTP processes that the strength of adhesion of the composite Ti/Au films to the substrate was

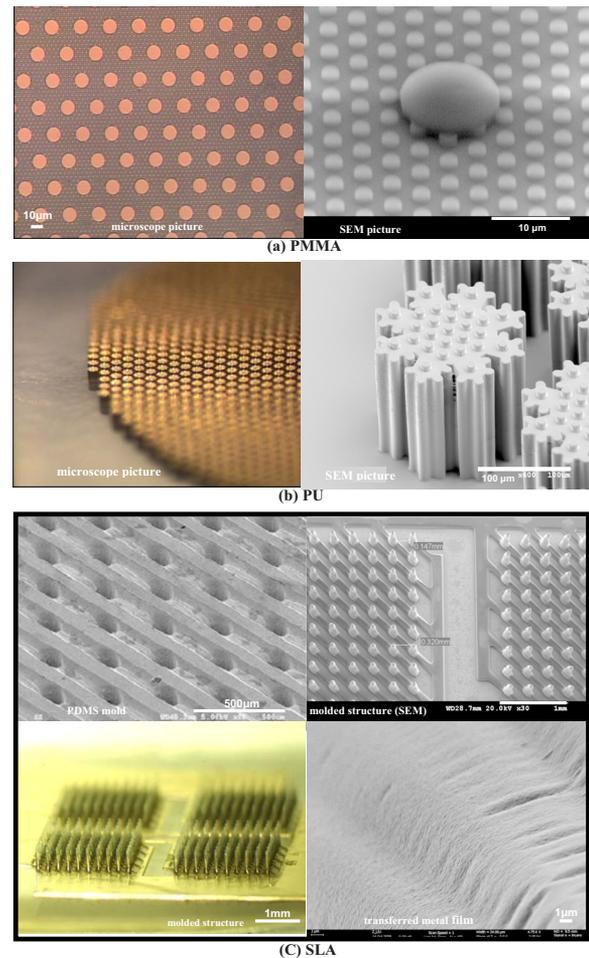


FIG. 2. (Color online) Molded 3D polymer structures with transferred metal patterns: (a) PMMA with 2 and 10 μm dimples (dimples are covered with transferred Au film), (b) PU with snowflake-like structures (snowflakes are covered with transferred Au film), and (c) epoxy resin (SLA) with high-aspect-ratio microelectrodes: (1) PDMS mold, (2) SEM picture of the molded structure, (3) microscope picture of the molded structure, and (4) SEM picture of transferred Au film.

greater than that of the bare Au film, and yields films with better structural integrity.⁷ Similarly, the transferring of multilayer metal films is investigated in this molding process. Au/Ti film using dc sputtering or e-beam evaporation is utilized and found to greatly improve the metal transfer efficiency with fewer cracking defects than the case of Au alone. Figure 2(c) shows a SEM image of the transferred metal film surface.

Although it has been demonstrated that noncovalent forces can be large enough to transfer gold from PDMS to other materials in the conventional nTP process, mild heating (50–80 $^{\circ}\text{C}$) is usually needed to reduce the transfer time from several days to hours.⁷ However for the replica molding process, the 3D metal transfer is in part a result of the solidification of the cast polymer. In some processes the metal transfer can be completed within a minute. For example, the epoxy-acrylate resins (Accura® si100) can be cured by high intensity UV light (10 mW/cm^2 for 50 s) and the gold film is completely transferred from PDMS after demolding. Furthermore, in the conventional nTP process, metal transfer to substrates with large surface roughness is less effective than a substrate with small surface roughness,^{7,8} while in this metal transfer molding process, there is no significant roughness effect observed in metal transferability as long as the

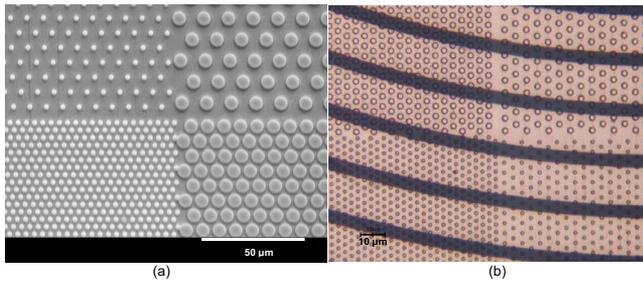


FIG. 3. (Color online) (a) Simulated “rough” surface with microdimples from 2 to 5 μm . (b) Au pattern is completely transferred from the rough PDMS surface to the cast polymer (PU).

liquid-state polymer conformally wets the interface during the molding step. To demonstrate metal transfer over a large rough surface, PDMS with simulated “roughness” of 2–5 μm [Fig. 3(a)] is coated with 30 nm Au film pattern and polymers such as SU8, PMMA, and PU are casted on the PDMS mold, and the Au film is found to be transferred from the PDMS to the case polymers completely [Fig. 3(b)]. Wrinkling and cracking are common defects in nTP processes. In our experiments, we found that metal film cracks and wrinkles due to the excessive strain during molding process can be effectively reduced by lowering the curing temperature to a mild range (under 80 $^{\circ}\text{C}$). Polymers that can be cured without heating, such as SLA and PU, have best quality of transferred metal films. In addition, high vacuum also helps speed up the molding process and reduce the potential metal film cracks due to the PDMS swelling by polymer solvent. However, polymers using aggressive heating or solvent for curing do generate cracks and wrinkles in the thin metal films, which is challenging for the metal-transfer-molding (MTM) process.

In most nTP process as well as the 3D metal transfer process, the thickness of the gold film is usually no more than several hundred nanometers because of possible cracking defects in thicker films. For the 3D metal transfer process, the uniformity is further limited by the deposition coverage on the PDMS stamps. For high-aspect-ratio structures (corresponding to the recessed region in the PDMS stamp), the bottom and sidewalls may suffer from insufficient film coverage.¹⁰ However, since the metal film from transferring shows comparable adhesion/strength to a directly deposited film, it can be used as a seed layer for further electroplating or electro-less-plating to achieve the desired thickness and uniformity. For example, the metal coatings for conducting currents or guiding electromagnetic waves are generally required to be uniform and relatively thick (usually more than one micrometer). A subsequent electroplating or electro-less-plating step is performed to yield the desired electrical functionality.¹¹

Similar to applying the nTP technique to the fabrication of contact electrodes on organic thin film transistors,^{6–8} we exploit as a fabrication example the application of the 3D metal transfer replica molding technique to organic microwave/millimeter-wave components. With the rapid development of wireless communication, there is an increased interest for low-cost MMIC or RFID. Organic materials such as liquid crystal polymer are rapidly emerging as an ideal

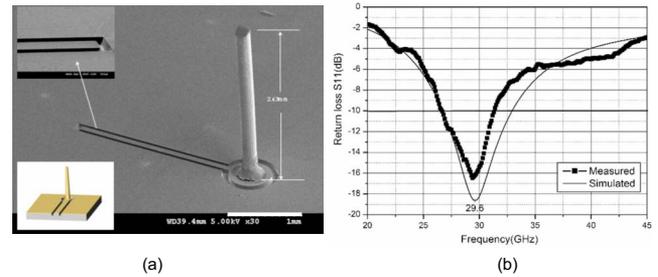


FIG. 4. (Color online) An organic CPW integrated with quarter wavelength monopole antenna by 3D MTM. (a) Fabricated monopole antenna structures by MTM. (b) Measured and simulated return loss (S_{11}) by Agilent 8510X vector network analyzer and Ansoft HFSS 10.0.

platform for low-cost, multiband, and reconfigurable rf front-end module integration. In this work, organic coplanar waveguides (CPWs) integrated with a monopole antenna are fabricated by the 3D metal transfer replica molding process. The topology of the organic micromachined CPW and monopole radiation antenna are shown in Fig. 4(a). In this structure, polymer layers can be patterned by molding to create the ground-signal-ground CPW configurations. The monopole antenna is simultaneously formed by metal transfer replica molding. The transferred metal film functions as a seed layer in a subsequent electroplating process by which the final metal layer thickness is 2 μm (above five times the skin depth at 30 GHz). S_{11} measurement is shown in Fig. 4(b), and greater than 16 dB return loss and over 18% bandwidth is achieved. Simulations show very close results to the measured resonant frequency and bandwidth.

In summary, this letter introduces an operationally simple metal transfer molding technique that is capable of metallization of 3D polymeric structures. The metal pattern is achieved by applying nTP to the PDMS stamp mold prior to the replica molding process. The transferred metal shows good fidelity regardless of the surface roughness of the PDMS-metal-polymer interface. It is also very promising in the applications of organic microwave circuits, micro-electrode-array, RFID, etc.

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