

3-D PATTERNED MICROSTRUCTURES USING INCLINED UV EXPOSURE AND METAL TRANSFER MICROMOLDING

Seong-O Choi¹, Swaminathan Rajaraman¹, Yong-Kyu Yoon¹, Xiaosong Wu² and Mark. G. Allen¹

School of Electrical and Computer Engineering¹, School of Polymer, Textile and Fiber Engineering²,
Georgia Institute of Technology,
Atlanta, GA, 30332, USA

ABSTRACT

We report a fabrication approach for three-dimensional (3-D) microstructures having functional metal patterns by using inclined UV lithography and 3-D metal transfer micromolding. Inclined rotational UV exposure using SU-8 has been exploited to simultaneously generate gradually varying 3-D structures with different heights in a single mask. For 3-D metal patterning, a metal transfer micromolding process has been utilized, where pre-patterned metal electrodes are formed on a polydimethylsiloxane (PDMS) mold prior to transfer, and these patterned metal structures are transferred to the molded 3-D microstructures during the micromolding process. Two approaches for metal pre-patterning have been utilized: one is selective metal removal by planar pattern transfer on an uneven surface and the other is pattern transfer using a shadow mask. Two test vehicles of 3-D patterned microstructures implemented by this process are demonstrated: an electroporation microneedle array and a 3-D microelectrode array (MEA). Insertion tests on pig skin using the fabricated microneedle array with different heights have been successfully performed, showing different penetration depths by fluorescent imaging.

INTRODUCTION

Recent advances in micromolding have enabled rapid progress in the cost-effective fabrication of three-dimensional (3-D) microstructures [1]. In general, the micromolding process consists of master structure fabrication, negative mold fabrication, and casting and separation. The fabrication of master structures often relies on advanced UV lithography using SU-8 for its complex 3-D structure capability [2]. As a mold material, PDMS has been widely utilized because of its mechanical compliance and faithful feature reproduction. In the conventional molding process, direct casting of a variety of polymers into the mold is performed to complete the process. In the case of *patterning* of metals on the three-dimensional surface to functionalize or enable other applications such as microelectrode arrays (MEAs) or an electrically active microneedle array for electroporation, either complex lithographic approaches [3], electrodeposited resists [4] or serial direct laser patterning [5] needs to be applied to the molded 3-D structures.

Alternatively, the 3-D micro electrodes can be formed during the molding process. The so-called *3-D metal transfer micromolding process* performs metallization and subsequent patterning on the PDMS mold prior to casting polymer, and these patterned metal structures are transferred to the molded 3-D microstructures during the molding process as shown in Figure 1. This process can be thought of as a three-dimensional extension of 2-D metal transfer processes used in nanoprinting [6], which exploits the difference in surface energy between PDMS and the microstructure material to enable metal transfer.

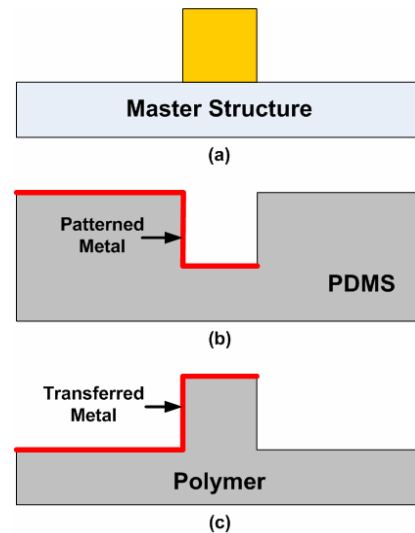


Figure 1. Concept of 3-D metal transfer micromolding: (a) Fabrication of a master structure, (b) Fabrication of PDMS mold from the master followed by metal deposition and patterning, (c) Formation of 3-D metal-patterned polymeric microstructure.

The process has several advantages. First, since metallization and metal patterning is performed on the mold structure, which is a negative form of the master structure, the process has an additional degree of freedom in 3-D metal patterning for the structures otherwise metal patterning may not be convenient with. Secondly, the pre-deposited or patterned metal layers contribute to enhancing moldability by increasing wettability on the mold surface for liquid polymer casting [7]. Third, the transferred metal does not necessarily require an intermediate adhesion layer as in conventional physical vapor deposition, further simplifying the process.

This paper consists of 3-D microfabrication using inclined UV lithography and micromolding for master structure fabrication, and subsequent 3-D metal transfer molding in which two metal patterning processes are demonstrated. The process is illustrated through two sample structures; one of the structures, an array of microneedles of varying heights, is tested for its insertion capabilities.

3-D MICROSTRUCTURE FABRICATION

A rigid SU-8 mold is fabricated using inclined UV lithography [8-10] to form negative concave shapes of various depths as shown in Figure 2a, b. Both mask dimensions as well as the incident angle of UV light determine the depth of the mold. This rigid mold is used to produce a mold master (Figure 2c) from

PDMS or other suitable material (such as Ni in the case of electroplating). The mold master is then used to create a flexible replica (Figure 2d) of the original rigid mold; this flexible mold should be made from PDMS due to both its low modulus and low surface energy. This flexible mold is then optionally metallized and patterned as described below. Polymer microstructures with various heights are then fabricated from the flexible mold (Figure 2e, f).

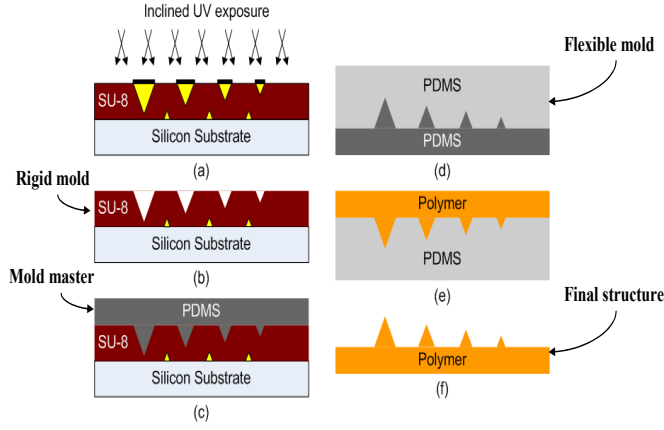


Figure 2. Fabrication steps for 3-D microstructure.

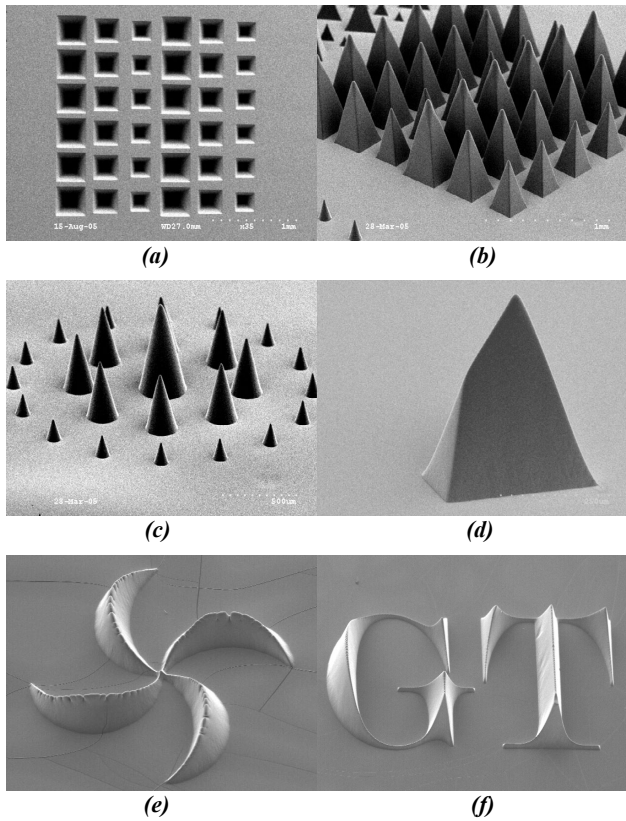


Figure 3. Fabricated structures: (a) rigid SU-8 mold, (b) variable height microneedle array cast from a flexible mold, (c) cone-shape microneedle, (d) beveled-tip microneedle, (e) vane-shape structure, (f) GT logo

Figure 3 shows various structures fabricated from inclined rotational exposure combined with the subsequent molding process. With differing mask shapes and inclination angles, molded copies of gradually-varying complex 3-D structures have been achieved. One application of interest for this technology is 3-D microneedle array fabrication. Advantages of this process include (1) easy control of the height and the tip angle of the microneedle by control of inclination angle; (2) simultaneous fabrication of microneedles of various heights by controlling the mask footprint; (3) no need for subsequent wet or dry etching for sharp tip fabrication.

3-D METAL TRANSFER MICROMOLDING

In 3-D metal transfer micromolding, metallization is performed on the negative form of the master made of PDMS. Two metallization schemes and subsequent 3-D metal transfer micromolding have been demonstrated. One scheme is to use selective metal removal from an intentionally formed non-planar mold surface using a 2-D metal transfer process. The other is to use selective metal deposition onto and into mold features using a shadow mask.

High Surface Energy Plate Approach: Figure 4 shows the fabrication steps using a selective metal removal process for an electrically functionalized molded electroporation microneedle array, which requires conductive microneedles and electrical isolations between needle rows. The PDMS mold is fabricated by a two-step SU-8 process and subsequent PDMS molding to form a protruding feature which will ultimately electrically isolate each row (a, b). After depositing Au on the mold (c), the Au layer on the protruding structure is removed by bringing a high surface energy plate in contact with the mold (d), transferring the metal on the protruding surface to the plate in a 2-D metal transfer scheme. UV-curable resin is then cast into the mold and optically cured (e). The pre-patterned Au layer is then transferred during the demolding process (f), resulting in the formation of a polymeric microneedle array with electrical isolations between needle rows (Figure 5). This process avoids the issues associated with conventional metal patterning, since conventional approaches will experience difficulties in patterning of the isolation layer on the bottom of the substrate due to the protruding needle structures.

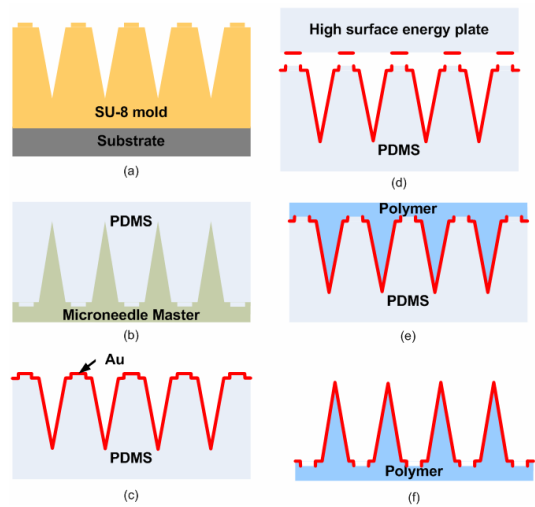


Figure 4. Fabrication steps for metal transfer onto a 3-D structure using a high surface energy plate

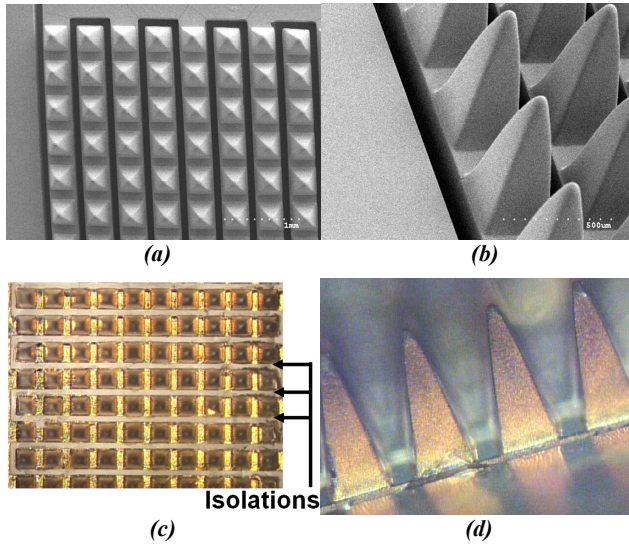


Figure 5. Fabricated microneedle arrays with applications in electroporation: (a, b) SEM of the mold master, (c, d) Optical photomicrograph of metal patterned structures.

Shadow Mask Approach: Metal can be patterned on the three-dimensional molds using a shadow mask approach. The shadow mask used in this paper was made from 125-150 μm thick Kapton sheets using excimer laser ablation. The ablation is achieved at 250mJ energy (20% attenuation) at the rate of 50-60 μm per cut. Feature sizes as small as 20 μm can be achieved using these parameters. This mask is then aligned with the PDMS mold (refer to section on 3-D Microstructures). Alignment marks are cut on the shadow mask to aid this process. The mask is held in position (proximity contact). This substrate is then loaded into a filament evaporator and Au/Cr (1 $\mu\text{m}/100\text{\AA}$) is evaporated. We have experimented with Au/Cr evaporation instead of just Au, because theoretically the adhesion force between Cr and cast polymer is higher than that between Au and polymer. However, it turned out that in both cases adhesion between the metal and polymer passes the Scotch tape test. SU-8 is then cast into this mold baked and blanket exposed. The SU-8 tower array is carefully peeled off from the PDMS mold after post-exposure baking. The Au/Cr metal layer is transferred from PDMS to SU-8 and becomes Cr/Au on the SU-8 structure in the case of both Au and Cr being evaporated. Due to the usage of shadow masks the towers have metal lines at various heights on them satisfying the 3-D metallization needed for improved MEA performance [11]. Also address lines to contact these electrodes are achieved to the end of the chip. The chip could potentially be mounted and wirebonded for use in MEA experiments. Figure 6 details the process steps and Figure 7 shows optical micrographs of the fabricated structures.

APPLICATIONS AND DISCUSSION

One application of interest for this technology is an electrically functional 3-D active microneedle array. The negative mold master has been fabricated using inclined rotational UV exposure with SU-8 as described in the previous section. Combined with the 3-D metal transfer molding process, cost-effective, mass-producible electrically active 3-D microstructures can be fabricated. These microneedles could be utilized as an electroporation microneedle array for either gene delivery through skin or electrochemotherapy of highly-localized solid tumors.

Other applications of interest include simultaneous local and systemic delivery of drug to blood vessels; drug delivery system through a cornea, which is not flat in nature; simultaneous measurement of biopotentials such as action potential at different sites (3-D MEA); and measurement of electrical properties of skin as a function of depth.

For these active microneedle applications, the strength of the needles and the ability to penetrate tissue has been tested. An array of microneedles with various heights that was made from biodegradable polymer, polylactic acid (PLA) has been used for pig skin *in vitro*. Red dye was spread on the pig skin, and a microneedle array was inserted with a force of approximately 10 N. After removing the microneedle array, the red dye on the surface was removed with deionized water. Cryosection microscopy was used to examine the cross-section of the pig skin (Figure 8), and showed that the microneedle array was successfully inserted with different penetration depths. The tip diameter of the microneedle array was less than 20 μm .

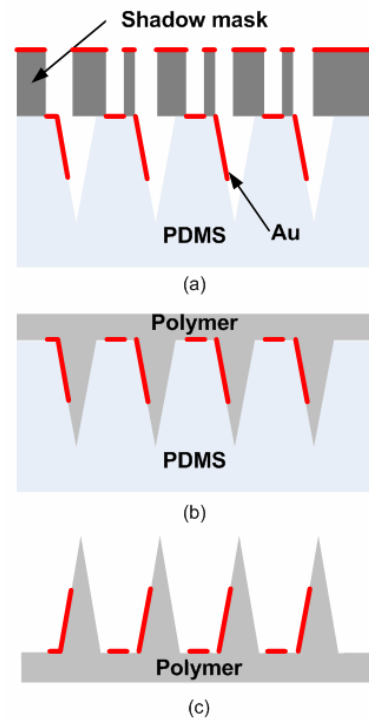


Figure 6. Fabrication steps for metal transfer onto a 3-D structure using a shadow mask

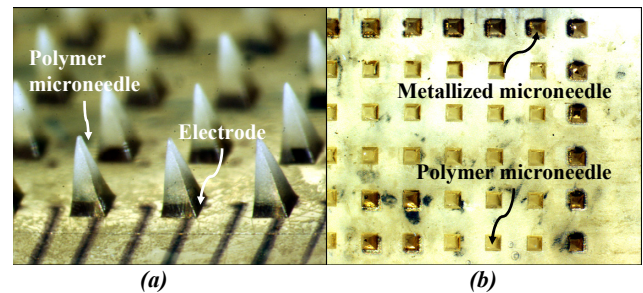


Figure 7. Fabricated micro-tower arrays: (a) electrodes with address lines and metal lines at various heights, (b) top view of the selectively metallized micro-towers

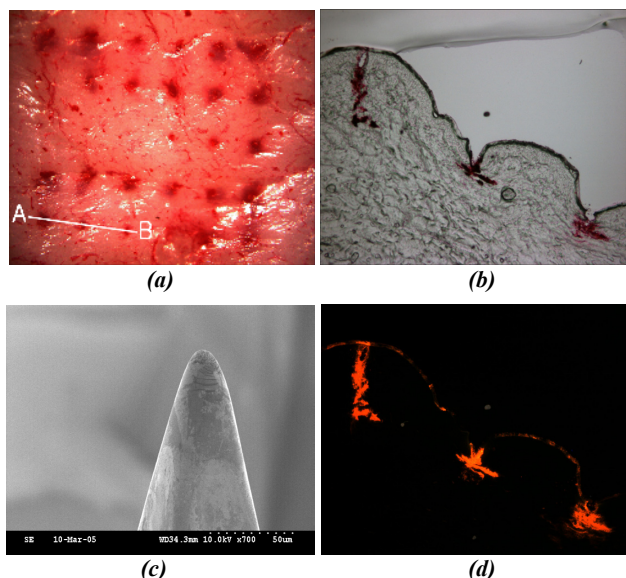


Figure 8. Optical photomicrograph of pig skin after insertion test with microneedle array of various heights: (a) visible light image (left: plan view; right: cross-section of A-B), (c) SEM micrograph of microneedle tip (scale bar indicates 50µm), (d) fluorescent light image of the cross-section showing 3 different penetration depths.

CONCLUSIONS

We have developed a technology for the fabrication of 3-D microstructures bearing metal patterns by combining inclined UV exposure and metal transfer micromolding. We have demonstrated two separate techniques for selective metal definition on the final structures: one using a high surface energy plate and the other using a shadow mask. In both these techniques metal has been selectively defined on the master mold and then transferred to the final structure during molding. This technology is potentially applicable to fabricate an electrically active microneedle array for either gene therapy or electrochemotherapy, 3-D microelectrode array for neural stimulation/recording, and so on.

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