ENHANCED WETTABILITY POLYMER MICROMOLDING BY A 3-D METAL TRANSFER PROCESS

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Introduction

Polymer based micromolding is capable of achieving complex three-dimensional (3-D) microstructures at low-cost and high-volume, with the added advantage that both microtexturing and the use of a large variety of materials are preserved. One of the key steps for successful micromolding is the fabrication of a suitable mold master. A special challenge exists where some applications have not only 3-D structure requirements, but also a high-aspect-ratio structural demand. For subsequent molding of many biological materials, for example hydrogel, aggressive processes such as repetitive freezing and thawing cycles may be required, placing severe robustness requirements on the mold-masters

SU-8, an epoxy-based ultra-thick negative photoresist, has been widely used for 3-D high-aspect-ratio applications because of its very low absorption in the near UV range. However, an SU-8 mold-master fabricated on a Si substrate (the so called SU-8/Si) often experiences mechanical failure after only a few mold uses due to the differing thermal and mechanical properties of the SU-8 and Si substrate. To overcome this mechanical weakness, the SU-8/Si mold-master (mother mold-master) can be replicated to a second mold-master (daughter mold-master) made of a single material for both the microstructure and the substrate using soft-lithographic replica molding.

Polydimethylsiloxane (PDMS) is extensively used as the negative mold in replica molding processes due to its high dimensional fidelity, chemical inertness, and ease of processing. However, the high surface hydrophobicity of PDMS often prevents the successful molding of high-aspect-ratio microstructures without the use of a specialized pressure or vacuum environment, which may cause structural deformation of the PDMS mold. To address this issue, efforts have focused on the modification of the hydrophobic PDMS surface to a hydrophilic SiO$_2$ surface by oxygen plasma, corona discharges, and UV-irradiation in combination with ozone treatments. However, this type of surface modification often promotes strong adhesion between the opponent parts, which increases the difficulty of the demolding step in the micromolding process.

In this work, an enhanced wettability replica molding process for unitary polyurethane (PU) daughter mold-master fabrication is proposed and demonstrated using a 3-D metal transfer technique in wafer-scale. In our approach, a thin gold layer is conformally deposited on the surface of the 3-D PDMS mold as a wetting layer before casting PU into the mold. Upon demolding, the gold layer is completely transferred to the PU surface. The gold-coated thermoset PU replica is a single piece structure, being mechanically rigid and robust. The transferred gold layer can perform additional functions in addition to wetting enhancement, including facilitation of mold separation, biocompatibility and enhancement to the chemical inertness of the molded part surface.

Experimental

Materials. SU-8, negative photopatternable epoxy resin (SU-8 2025 and SU-8 5, MicroChem, Co.) was used. Polydimethylsiloxane (PDMS, Sylgard 184) was purchased from Dow Corning Co. Polyurethane (Task 3) was purchased from Smooth-On Inc.

Instrumentation. Karl Suss MA-6 Mask Aligner was used to align and to expose SU-8; CVC DC sputterer was used to deposit gold film on the PDMS surface.

Microstructure configuration. The surfaces of the mold master consist of approximately 1900 micro protrusions within a circle of 15 mm diameter, where each protrusion is shaped as a snowflake and its nominal diameter is approximately 150μm and height 150μm. Each snowflake has salient patterns along with the sidewall in the size of 10, 5, and 2μm, and protruded patterns at the top surface with varying dimensions and heights of 10, 5, and 2μm. The salient sidewalls and the protrusions are intended to stimulate cell growth as well as to provide better cell adhesion to the mold.

Two-step SU-8 lithography (mother mold-master fabrication). A two-step SU-8 photolithography process is used and described in Figure 1. First, a 150μm-thick layer of SU-8 (SU-8 2025) is spin-coated on a 4 inch silicon wafer (1a). After soft-bake, the SU-8 is exposed to form the snowflake structure, followed by a post-exposure bake (PEB) to cross-link the snowflake structure (1b). After cooling down, a second thin SU-8 layer (10, 5 or 2μm thick, SU-8 5) is spin coated on top of the first layer of SU-8 (1c). After soft-bake, the thin SU-8 layer is exposed with alignment to form the small protrusion structures, followed by PEB (1d). The two layers of SU-8 are developed in a single-development step to complete the master pattern.

3-D metal transfer micromolding (daughter mold-master fabrication). Figure 2 illustrates the micromolding process of a unitary daughter mold-master. PDMS is cast against the SU-8/Si master and then cured at room temperature. The PDMS mold is peeled off and then coated on top of a glass plate for ease of handling. A 100-nm-thick gold layer is conformally deposited on the PDMS mold using DC sputtering (2a and Figure 5). PU oligomers are mixed and cast into the PDMS mold (2c) and cured. Upon separation of the cast PU part from the PDMS mold, the deposited gold layer is completely transferred to the PU side.

Results and Discussion

Two-step SU-8 lithography. Figure 3 shows the successfully fabricated SU-8/Si mold-masters bearing 10, 5, and 2μm protrusions, respectively. Due to the mismatch of the coefficients of thermal expansion of the SU-8 and the Si substrate, the SU-8 microstructures are often delaminated from the Si substrate as shown in Figure 4.
3-D metal transfer micromolding. Figure 6 shows the successfully replicated gold-coated PU structures bearing 10, 5, and 2 µm features on the 150 µm snowflake with high fidelity. Figure 7 shows the different length scale of the PU structures (from left): a 4 inch wafer scale, a unit array of 15 mm in diameter, a magnified snow-flake array, and a single snowflake bearing salient features of 5 µm on the sidewall and protrusions on the top surface.

Figure 5. Elastomeric PDMS mold coated with 100nm gold: column wells with 10µm, 5µm, and 2µm salient features on sidewall and dimples on the bottom (corresponding to Figure 2b )

Figure 6. PU structure from Au coated PDMS mold with metal transfer with 10, 5, and 2µm salient features on sidewall and protrusions on the top surface (from left)

Figure 7. Unitary PU daughter master structures in 4-inch wafer scale

Since the surface energy of the PDMS (19.8 mJ/m²) is extremely low, PU (surface energy: 43 mJ/m²) is unlikely to wet the bare PDMS mold surface, resulting in only partial replication of the snowflake columns as shown in Figure 8a. In contrast, gold layer deposition greatly increases the hydrophilicity of the PDMS surface. As a way to modify the PDMS surface, gold deposition is especially suitable for the molding process compared to either chemical modification, or surface treatment by plasma, or UV/ozone, since the gold layer neither adheres to the PDMS surface nor reacts with the casting material. Thus, the gold layer acts as both a “wetting” and a “separation” layer in the molding process. Figure 8b shows gold-coated PU structures replicated using the 3-D metal transfer technique demonstrating the successful daughter mold-master fabrication with high fidelity.

Figure 8. (a) PU cast from a PDMS mold without gold coating, (b) PU cast from the gold-coated PDMS mold with 3-D metal transfer

The mechanism of metal transfer from the PDMS mold to the PU replica lies in the difference of adhesion strength between the PDMS-Au and PU-Au interfaces. Two-dimensional metal transfer from substantially planar PDMS surfaces to other substrates has been studied and known as a nanotransfer printing (nTP) process, where the self-assembled monolayers (SAMs) function as covalent “glues” and “release” layers for transferring material from relief features on a stamp to a substrate. This technique is limited to systems in which specific covalent interactions guide the transfer of the metal from the surfaces of the PDMS to the substrates. Later, research work showed that non-covalent surface forces can be large enough for metal to transfer from PDMS to polymers, yet without an adhesion promoting layer such as titanium, the transferred gold layer does not often show good adhesion to the polymer surface. The metal transfer molding technique described here extends the non-covalent 2-D metal transfers to 3 dimensions, during which the gold layer functions as the SAM layer. Moreover, it shows improvement of the adhesion between the metal and the polymer surface. The transferred Au film withstands a Scotch™ tape adhesion test, which suggests strong adhesion between transferred Au and cast PU, perhaps enhanced by mechanical interlocking effects of the occupancy of the defects of the Au film by small molecules of PU oligomers.

Due to the low viscosity of the cast PU oligomer (160 cps), complete filling of the high-aspect-ratio structure can be achieved without external vacuum or high pressure. Moreover, by virtue of the 100% solid material used in the reacting system, excellent dimensional fidelity can be obtained. Besides these merits, reactive casting of thermoset polymers allows variety in the choice of materials, low cost, and solvent resistance. In addition to PDMS and PU, other thermoset polymers that are potential candidates for metal transfer reactive casting include unsaturated polyesters, epoxies, polyurethane acrylates, etc.

Conclusions

A SU-8/Si mold master with 3-D high-aspect-ratio microstructures was fabricated with high yield using a two-step SU-8 lithography process. A wafer-scale 3-D metal transfer micromolding technique was demonstrated to fabricate unitary thermoset secondary mold-masters for a cell-culturing scaffold. Thin gold layer deposited on PDMS mold greatly enhanced the wettability of the PDMS surface, while it also acts as a “glue” and a “separation” layer during the metal transfer micromolding. The transferred gold layer enhances the biocompatibility and the chemical inertness of the molded part surface.

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References