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Replication of Two-Photon-Polymerized Structures with Extremely High Aspect Ratios and Large Overhangs

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We demonstrate the replication of 3-D structures created with an acrylic polymer using multiphoton absorption polymerization. Microtransfer molding was used to replicate complex structures rapidly and with high fidelity, including structures that have high aspect ratios or reentrant features. It is also possible to replicate large numbers of structures simultaneously.

Multiphoton fabrication is gaining increasing attention as a technique for the creation of complex, 3-D structures that cannot be created with conventional lithography.[1−10] This technique relies upon the fact that the probability for the simultaneous absorption of *n* photons by a molecule is proportional to the light intensity to the *n*th power. As a result, it is possible to localize absorption to within the focal volume of a laser beam that has been focused tightly through a microscope objective.[11] If the absorption of light leads to an appropriate photochemical or photophysical change in the material being irradiated, then by scanning the position of the laser beam in the medium it is possible to create intricate 3-D structures. Furthermore, if chemical nonlinearity is present, then the resultant intensity threshold for fabrication can make it possible to create features that are considerably smaller than would be expected from the diffraction limit. Multiphoton absorption polymerization (MAP) with 800-nm light, for example, has been used to create 3-D structures with feature sizes as small as 120 nm.[4]

Despite its unique capabilities, one drawback of MAP is that it is an inherently serial technique. Fabrication is a voxel-by-voxel process, and it can take many minutes to hours to form a single complex structure. This problem effectively precludes the direct mass production of structures using MAP.

Microtransfer molding[12,13] (μTM) is a soft lithographic technique that is an increasingly popular means of replicating microscopic structures. In its usual implementation, μTM begins with the spin coating of a polymeric photoresist on a flat substrate. The photoresist is exposed through a mask, and the unexposed regions are washed away with solvent to leave behind a master composed of hardened photoresist structures. The substrate is then covered in poly(dimethylsiloxane) (PDMS), which is subsequently cross linked to form an elastomeric solid mold that can be peeled away from the master. The mold can be filled with a molding material and pressed against another substrate. Curing of the molding material produces a replica of the original structure. Not only can numerous high-fidelity replicas be made from one mold but many molds can be made from a single master structure as well.

Here we demonstrate that μTM can be used for the rapid, high-fidelity replication of complex 3-D polymeric master structures created via MAP. The marriage of μTM with MAP effectively turns the creation of arrays of complex 3-D microstructures into a parallel lithographic process. We further use MAP to test the limits of μTM for replicating challenging 3-D structures, such as those with extremely high aspect ratios or significantly reentrant features.

The creation of complex structures using MAP follows a procedure similar to one that we have reported previously,[8] so we describe it only briefly here. For MAP fabrication, we employed an acrylic resin that is composed of 48 wt % ethoxylated(6) trimethylolpropane triacrylate (Sartomer), 49 wt % tris(2-hydroxyethyl)isocyanurate triacrylate (Sartomer), and 3 wt % Lucirin TPO-L (BASF). After thorough mixing, the resin is placed in a cell consisting of a microscope slide treated with (3-acryloxypropyl)trimethoxysilane, a 100-μm-thick spacer, and a cover slip. The excitation source is a Ti:sapphire laser (Coherent Mira 900-F) producing 100-fs pulses with a center wavelength of 775 nm at a repetition rate of 76 MHz. The beam is expanded to overfill the back aperture of a 40×, 1.3-NA oil-immersion objective (Zeiss Neofluar) on an upright microscope. The position of the focal point of the laser relative to the sample is controlled using a motorized microscope stage (Ludl Bio-Precision). Typical fabrication powers are <5 mW. In the case of the 300-μm tower described below, a 500-μm-thick spacer, a 10×, 0.3-NA nonimmersion objective, and 20 mW of power were employed. In all cases, the unexposed resin was washed away with ethanol after fabrication.

For replication, a few grams of Sylgard 184 (Dow Corning) are mixed in a 10:1 mass ratio of prepolymer and curing agent. The resulting mixture is then centrifuged for several minutes to remove air bubbles. A lightly greased O-ring is placed around the structure, and the PDMS is poured in to fill the O-ring such that a typical final mold is 3 mm thick and 1 cm^2 in area; these parameters are not critical to the success of the molding. The

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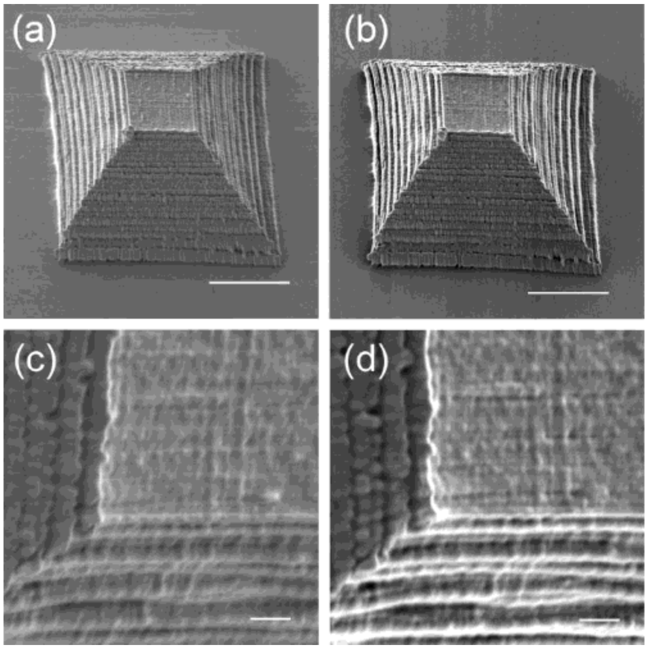

Figure 1. Replication of simple structures created via MAP. Images a and b show the original and the 15th replica of a truncated pyramid; the scale bars are 10 μm in length. Close-up views of the original (c) and replica (d) demonstrate the fidelity of the molding of submicrometer features, even after many generations; the scale bars in these images are 1 μm in length.

sample is then placed in an oven at 150 °C for 15 min, after which the PDMS mold is carefully peeled off of the substrate with tweezers. Replicas are typically made by pouring the same acrylic resin formulation used to make the initial microstructures into the mold, removing any excess resin with dry air, and pressing the mold against a flat glass substrate. The sample is then set under an ultraviolet lamp for 30 min. After the curing of the molding material, the mold is peeled off of the hardened replica. Typical peeling times and angles are on the order of 3 s and 10 to 60°, respectively. All structures reported here could be replicated completely reproducibly without using special care in determining these parameters. However, typically peeling angles on the smaller side of this range were used for towers, and those on the larger side of this range were used for structures with opposing overhangs. Presumably, the range of structures that can be replicated reproducibly could be increased further by a careful study of the effects of the peeling rate and angle.

To test the ability of μTM to replicate acrylic master structures, simple test structures were created using MAP. PDMS was found to cure satisfactorily when in contact with such structures. Parts a and c of Figure 1 show, respectively, low- and high-magnification scanning electron micrographs (SEMs) of a representative master structure created using MAP, a truncated pyramid. A single PDMS mold of this object was found to be capable of creating many replicas before its quality degraded. For instance, parts b and d of Figure 1 show low- and high-magnification images of a 15th-generation replica of the master structure. The replica is virtually indistinguishable from the original, and even submicrometer features have been replicated with high fidelity. In the low-magnification image of the replica, there is some evidence of bowing at the base (i.e., the edges of the replica are slightly concave with respect to those of the original; this effect increases with further replication). This phenomenon is probably due to the slight absorption of the prepolymer resin into the PDMS in the mold and can presumably be avoided by using a different molding material.

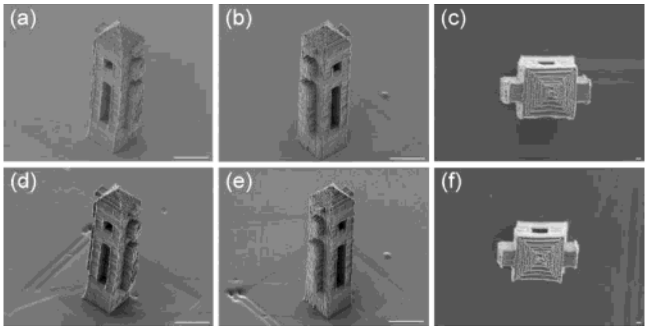

Figure 2. Replication of a complex structure with reentrant features and protrusions. (a−c) Three views of the original structure. (d−f) Three views of a replica of the structure. The scale bars are 1 μm long in c and f and 10 μm long in the other panels.

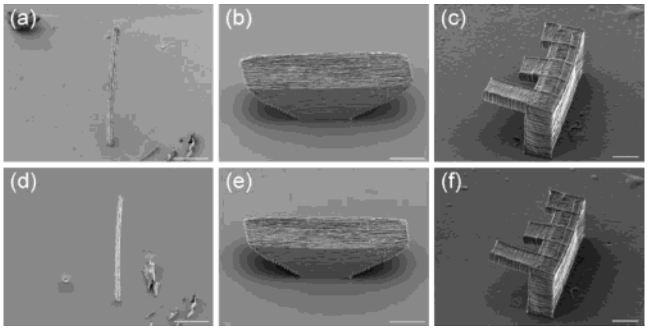

Figure 3. Master structures with high aspect ratios and large overhangs (a−c) and their replicas (d−f). Images a and d are a 300-μm-high tower that is 10 μm on a side; the scale bars are 100 μm in length. Images b and e are a structure with opposing 60° overhangs that jut out 10 μm each; the scale bars are 10 μm in length. Images c and f are a series of three cantilevers with lengths of 5, 10, and 20 μm; the scale bars are 10 μm in length.

It has been demonstrated previously that μTM is capable of reproducing reentrant structures with overhangs.[14] The replication of such structures is possible because the elasticity of PDMS allows it to pull away from cavities or overhangs when being released from a structure. Although reentrant structures are difficult to create with standard lithographic techniques, they can be fabricated readily with MAP. To test the ability of μTM to replicate reentrant structures, we therefore designed a complex tower with sizable protrusions and cavities. Parts a−c of Figure 2 show SEMs of the original tower structure taken from different vantage points, and parts d−f of Figure 2 show SEMs of a replica of this structure from the same vantage points. It is clear that the entire structure has been reproduced with high fidelity, including all of the reentrant features.

The successful μTM replication of structures with aspect ratios as high as 15:1 that were fabricated using the LIGA process has been reported.[15] Although these structures were tall, they were wall-like and so were narrow only in one dimension. The fabrication of tall structures that are narrow in two dimensions is difficult with standard lithographic techniques but is straightforward to accomplish using MAP. The replication of such structures is considerably more challenging than the replication of tall walls, so such tower-like structures were explored as masters for molding. Figure 3a is an SEM of a tower that is 300 μm high and is 10 μm wide in each of the other two dimensions. As shown in Figure 3d, despite the 30:1:1 aspect ratio of this structure, it can be reproduced with high fidelity and remains attached to the substrate when the mold is detached from it.

Figure 3b shows an SEM of a master structure with opposing overhangs that jut out by 10 μm and have an undercut angle of

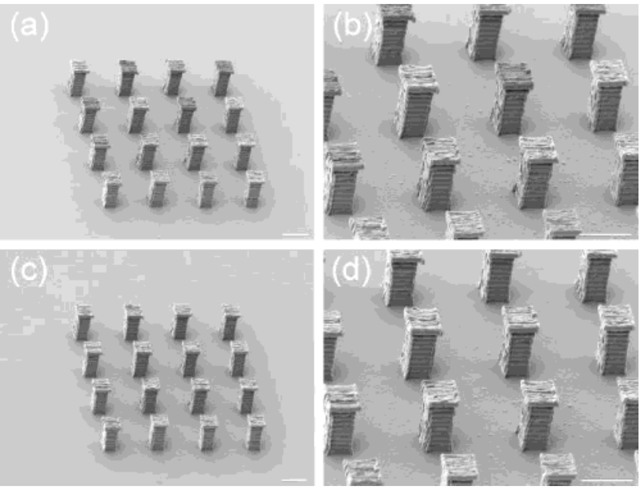

Figure 4. Views of a 4 × 4 master array of towers (a, c) and a replica (b, d). Scale bars are all 10 μm.

60° from the vertical. It is significant that this structure has opposing undercuts that require the mold to stretch to release the master structure regardless of the direction in which it is removed. However, as shown in Figure 3e, this structure can still be replicated with high fidelity using μTM.

Having determined that structures with undercuts at a high angle can be replicated, we investigated whether structures with 90° overhangs could also be molded. Figure 3c is an SEM of a wall on which 2.5-μm-thick cantilevers with lengths of 5, 10 and 20 μm and a width of 10 μm have been fabricated. As shown in Figure 3f, these cantilevers proved possible to replicate as well. Cantilevers longer than 20 μm could not be replicated reproducibly, however. No attempt was made to optimize either the thickness of the cantilevers or the properties of the PDMS, and we believe that such an optimization would allow for the replication of structures with even longer overhangs.

Potential applications of MAP-fabricated structures will generally require that a large number of structures be created on a single substrate. It is therefore important that μTM be capable of replicating arrays of structures. Parts a and b of Figure 4 are low- and high-magnification SEMs of an array of 16 towers with overhanging lips at their apexes. As shown in parts c and d of Figure 4, μTM is readily capable of replicating this tower array.

We have demonstrated that μTM is an effective technique for the rapid replication of polymeric structures created via MAP. A single array of master structures can potentially be used to create hundreds of molds, each of which can be used to create hundreds of replicas of the master. If desired, a replica can also serve as a master for the creation of new molds. The creation of a master array with MAP followed by replication with μTM is directly analogous to the fabrication of masks with direct laser writing followed by the use of these masks in photolithographic patterning. Furthermore, structures replicated with μTM need not be composed of the same material as the original, and it is therefore possible to create structures made of materials for which direct multiphoton fabrication may not be possible. Although it is not possible to use μTM to replicate every structure that can be made with MAP, the results presented here demonstrate that the topological constraints for replication are considerably less severe than might have been imagined. The ability to replicate complex 3-D structures should help to increase significantly the range of applications in which MAP can be employed.

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