Two-Photon Three-Dimensional Microfabrication of Poly(Dimethylsiloxane) Elastomers

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Three-dimensional (3D) microfabrication by two-photon-initiated chemistry takes advantage of the spatial selectivity of two-photon absorption (TPA)[1,2] to fabricate 3D polymeric structures.[3−5] By scanning the focal point of a laser within the bulk of a photosensitive material, a chemical change is induced, allowing the formation of arbitrarily complex patterns with sub- to single-micrometer resolution. To date, much of the work in two-photon 3D microfabrication has been restricted to radical-initiated polymerization of acrylates as a means to optimize and establish the capabilities of the technique, with an eye toward its use in applications such as microelectromechanical systems, microfluidics, and photonics. To this end, several studies have been conducted involving materials with properties tailored to specific applications, such as biocompatible materials for sustained delivery devices,[6] polymers doped with magnetite nanoparticles for actuated microstructures,[7] photoresponsive hydrogels for micro-optical mechanical devices,[8] and organic−inorganic hybrids with tunable refractive indices for photonics.[9]

This work describes two approaches for creating poly-(dimethylsiloxane) (PDMS)-based microstructures by two-photon 3D microfabrication via photohydrosilylation and radical-initiated cross-linking. The elastomeric nature of PDMS makes this material a departure from the "hard" cross-linked materials that typically result from this technique. To the best of our knowledge, neither PDMS nor photohydrosilylation have been used in a high-resolution imaging/stereolithographic application, including two-photon 3D microfabrication. PDMS microstructures are of interest due to their compatibility with current microfluidic device fabrication; an area

which is currently dominated by replica molding of thermally curable PDMS.[10] Preparation of elastomeric PDMS microstructures by two-photon 3D microfabrication may be useful for modifying generic microfluidic channels to add a higher level of functionality or to build complex 3D microfluidic networks which are either difficult to prepare or are totally inaccessible using conventional molding techniques.[11,12] The utility of topographically modified microfluidic channels has been demonstrated by the use of arrays of microstructures on the floor of channels to sort biomolecules[13] and aid in the mixing of solvent streams.[14,15]

PDMS-based microfabrication typically employs thermally initiated, platinum-catalyzed hydrosilylation to cure a viscous liquid composed primarily of dimethyl-vinyl-terminated PDMS, poly(methylhydrosiloxane-*co*-dimethylsiloxane), and dimethylvinylated silica into a tough, elastomeric solid.[16] The photoactive component most commonly employed in photohydrosilylations is (η^5-cyclopentadienyl)trialkylplatinum, which decomposes upon UV irradiation to yield the active hydrosilylation catalyst, a heterogeneous platinum colloid.[17,18] Photohydrosilylation has been previously used in bulk curing of PDMS-based materials to prepare solvent-free adhesives, coatings, dental materials, and gaskets.[19−21] To assess the utility of (η^5-cyclopentadienyl-methyl)-trimethylplatinum as a two-photon absorbing initiator, it was loaded into the uncured PDMS-based liquid at 0.7 wt % and exposed at 710 nm.[22] A refractive index change of the exposed material indicated that curing had been initiated in the regions exposed to light. Subsequent development by rinsing with ethyl acetate confirmed the formation of finely resolved microstruc-

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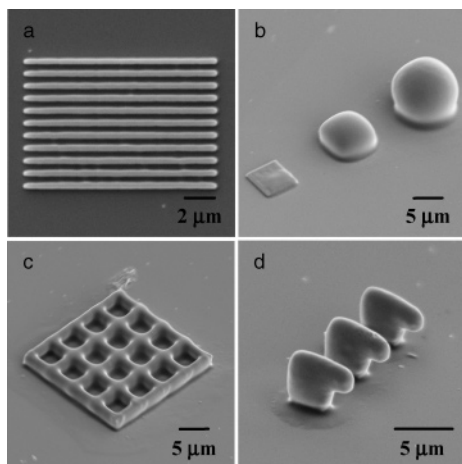
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 (16) PDMS [Sylgard 184 (Dow Corning)] is widely used in microfluidic device fabrication. A related material, Sylgard 182 is employed in these studies because it contains a fugitive agent to increase the pot-life. According to the manufacturer, both materials require the same thermal treatment for curing and do so to give materials with the same properties.
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 (22) The instrument employed for the two-photon 3D microfabrication is an Olympus IX70 microscope with a Lambda Physik Ti: sapphire laser (∼80 MHz, ∼200 fs pulse width) which is focused on the sample through an oil immersion objective lens (NA = 1.35). Motorized mirrors and stage are used to control the position of the beam on the sample. Laser powers were measured using a Spectra-Physics 407A powermeter. Exposures are performed voxel by voxel with each voxel separated by 0.213 μm in the *x,y*-plane and 0.7−1.0 μm in the *z*-plane, and exposure times of greater than 100 ms/voxel. A few drops of the resin were placed on a microscope cover slip (No. 1) for use in the microfabrication experiment.

Figure 1. (a) Lines with ~350 nm thickness and an aspect ratio of ~1.7. (b) Microstructures composed of 1, 5, and 10 layers (left to right). (c) Microcells, each $3 \times 3 \mu$m wide and 2.6 μm deep. (d) Array of cantilevers.

tures with line widths as low as 350 nm (Figure 1a). These results were confirmed to be due to a multiphoton process by the fact that they were not initiated by the same laser powers when delivered in a continuous manner instead of a pulsed one. This material has a useful fabrication range of 1.9–3.0 mW at a scan rate of 100 ms/voxel. This system is slightly less sensitive and has a narrower useful range than a number of commercial resins employed in this lab under similar conditions.[23]

A noteworthy feature of two-photon 3D microfabrication with this material is a thermal component to the curing process which results from the behavior of (η^5-cyclopentadienyl-methyl)trimethylplatinum as a thermal initiator of the hydrosilylation reaction. Although isolated lines with aspect ratios of >3 and single voxels with lateral and axial dimensions of 0.5 and 1.1 μm, respectively, have been achieved, thermal curing tends to lower the resolution obtainable with this material when longer exposure times are employed or when many voxels are closely packed. This phenomenon is illustrated in Figure 1b in which a square composed of a single layer of voxels has a well-defined shape but takes on a rounded appearance when 5- and 10-layer structures are prepared. Interestingly, the thermal component to the curing process can be exploited to improve adhesion between an existing PDMS surface and a photocured sample of PDMS via a subsequent thermal treatment (120 °C, 10 min), such that the two components cannot be separated without damaging the material. Further examples of microfabrication using this system are shown in Figure 1c and d, with an array of micro-cells and cantilevers, respectively.

A radical-initiated curing approach employing the same PDMS-based resin was investigated in an attempt to prepare a material with less thermal sensitivity and therefore improved photoimaging properties. Radical-initiated cross-linking of PDMS materials between all possible combinations of vinyl and methyl groups have been reported.[24] Isopropyl-thioxanthone, a well-known
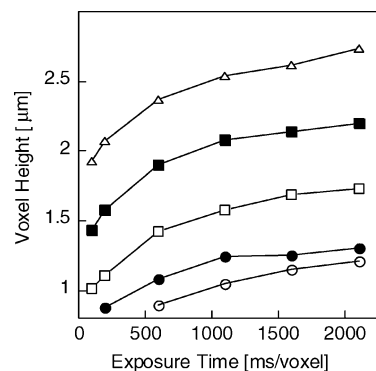

Figure 2. Power and exposure time dependence of voxel height 2.5 mW (○), 3.1 mW (●), 3.9 mW (□), 6.5 mW (■), 8.2 mW (△).
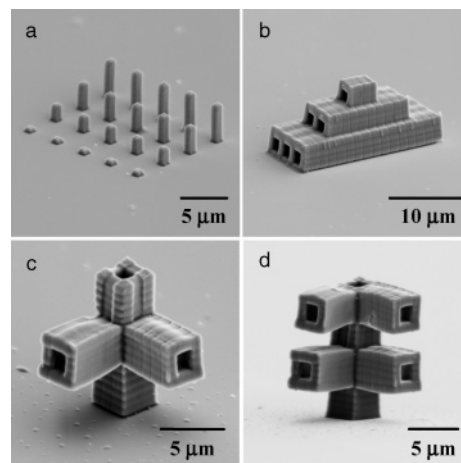

Figure 3. (a) Array of $1 \times 1 \mu$m pillars the largest of which is 4 μm tall. (b) A stack of microcapillaries of various lengths with inner diameters of <2 μm. (c and d) Microcapillary intersections.

radical initiator used in UV curing technologies[25] and in two-photon 3D microfabrication,[7,26] was loaded into a formulation of the uncured PDMS-based resin at 0.4 wt % and exposed at 780 nm. After development with ethyl acetate, finely resolved structures were obtained and were shown to result from a multiphoton process which did not have the thermal dependence associated with the photohydrosilylation samples. This material had a useful fabrication range of 3.9–8.2 mW at a scan rate of 100 ms/voxel. The power and exposure-time dependence on the height of a line of adjacent voxels appears in Figure 2. As indicated there, higher powers and longer exposure times act to increase the number of radicals generated locally and result in an increase in voxel sizes. The width of the corresponding single voxel lines varies from 0.3 to 0.6 μm over the same ranges of power and exposure time such that single voxels have aspect ratios of 3–4. Characterization of the microfabrication process in this way allowed for the preparation of a variety of microstructures designed to demonstrate the performance of this system as a high-resolution imaging material and its potential utility in microfluidic systems (Figure 3a–d).

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Two photocuring approaches for making PDMS-based microstructures by two-photon 3D microfabrication have been presented and characterized in terms of their utility in microfabrication processes. It should be noted that there are other methods and mechanisms for the photocuring of silicon-containing polymers and these are at present unexplored for two-photon microfabrication.[27–29] Thus, the strategies reported here should be viewed as examples of the sorts of microfabrication processes possible and may prove useful for building complex structures impossible with current micromolding methods or as a complement to existing PDMS device fabrication via replica molding to achieve a higher level of functionality than is otherwise possible.

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