Lithographic patterning on polydimethylsiloxane surfaces using polydimethylglutarimide†

Roger M. Diebold*ab and David R. Clarkea

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We present a method for high fidelity lithographic patterning on polydimethylsiloxane (PDMS) surfaces employing traditional cleanroom equipment and commercially available materials that overcomes previous problems in PDMS processing. To illustrate this method, an electrostatically actuated microfluidic pump and rectangular diffraction gratings were fabricated on PDMS.

Polydimethylsiloxane elastomers have gained increasing attention as a materials system for developing chip-scale microfluidic and microelectromechanical devices. However, a major limitation of PDMS is the difficulty in performing traditional lithography on its surface. The low surface energy of PDMS (23 mN m⁻¹), originating from the flexible siloxane backbone and pendant methyl groups, is only slightly higher than that of Teflon (19 mN m⁻¹), which results in a tendency for Novolak-based photoresists to dewet upon application. Cracking can also be problematic due to the high coefficient of thermal expansion (CTE) mismatch between PDMS and photoresist.

Several approaches currently exist for lithographically patterning on cured PDMS, each having drawbacks which limit the type and function of the resulting devices. Researchers have patterned photoresist on top of various adhesion layers to create shadow masks, but these methods necessitate alterations of the PDMS surface which are often undesirable. For example, evaporated metal can be applied as an adhesive layer, but the spontaneous buckling of the metal film results in long-term and undesirable PDMS surface topography. Similarly, parylene can also be evaporated onto PDMS, but dry etching is necessary to transfer the pattern, which can damage the underlying PDMS surface. Novolak-based photoresists can be directly applied to PDMS but only after surface treatment with oxygen plasma, known to create a thin, rigid silicate layer that buckles in a manner similar to that of evaporated metal films. Oxygen plasma treatment of PDMS temporarily creates hydrophilicity by stripping methyl groups from the surface and forming silanols, but hydrophobicity returns within a matter of hours due to the low molecular weight siloxane chain migration to the surface.

Liquid polyimide has also been spin coated on PDMS but likewise requires oxygen plasma treatment prior to application. Other patterning methods for PDMS are available, such as photodefendable silicones, but the resolution of these materials is on the order of 10 μm which is limiting for some applications.

Soft lithography is a popular method for rapidly producing patterned PDMS surfaces but requires oxygen plasma treatment to bind the PDMS to other silanol functionalized surfaces. In addition to surface buckling concerns, oxygen plasma bonding has been shown to be inconsistent in performance and variable in strength. Feature alignment in multilayer soft lithography is considered to be relatively poor as it is typically performed manually. We present an alternative method of high resolution photolithographic patterning on PDMS which alleviates many of the problems associated with existing methods.

Polydimethylglutarimide (PMGI) is a commercially available positive tone photoresist which is typically used in combination with high resolution Novolak resists in bi-layer liftoff processes. We find that the adhesion between PMGI and PDMS is sufficient to permit high resolution lithography without any surface modification. Although mainly employed as a deep ultraviolet resist in conjunction with a Novolak imaging resist, PMGI can also be used as an electron beam and X-ray sensitive resist on its own. The processing method presented in this technical note allows for traditional photolithographic patterning of resist shadow masks on cured PDMS, a method which is fully compatible with standard cleanroom exposure equipment such as contact aligners, steppers, electron beam exposure, or X-ray exposure tools, thereby enabling the fabrication of extremely high fidelity and precisely aligned features. PMGI is also completely solution processable and easily removed by photoresist strippers, unlike epoxy-based resists. Multi-layered structures can also be created through successive applications of PDMS on patterned PMGI. The high resolution and registration capability of this process are particularly advantageous relative to patterning methods currently available because of its compatibility with modern exposure tools and solution processability.

To illustrate the utility of PMGI lithographic patterning, we present the fabrication methodology for defining compliant...
electrodes on a PDMS surface for use in a microfluidic pump. Electrodes are deposited on the top side of a PDMS encapsulated, fluid-filled channel and when subjected to a potential difference relative to a conductive substrate, the top surface deflects downward, locally displacing fluid. A series of electrodes have been designed such that actuation in sequence down the length of the channel produces a peristaltic motion which forces fluid in the desired direction. To further demonstrate the versatility of this processing technique, 1- and 2-dimensional rectangular diffraction gratings have been fabricated directly on PDMS.

The processing method for the peristaltic pump, as illustrated in Fig. 1, is as follows (ESI†). Conductive silicon wafers were spin coated with a SPR 220–7.0 photoresist, softbaked for 3 minutes on a hotplate at 115 °C, and cooled to room temperature in air. The channel patterns were exposed and left for 5 minutes until the photoreaction was complete. The sample was developed until no further color change was observed. To prevent premature channel collapse later on, the photoresist was rounded by heating at 120 °C. PDMS mixed in a 15 : 1 ratio by weight (base : cure agent) was spin coated, degassed, then cured in an oven at 65 °C for 2 hours. PMGI SF-11 was spin coated on the PDMS surface. Without baking the PMGI, S1813 imaging resist was spin coated and the sample was softbaked at 70 °C for 2 minutes on a hotplate. This low temperature baking step is critical in avoiding PMGI/photoresist cracking as it removes enough solvent to prevent nitrogen formation during exposure, but not enough to completely embrittle the resist. Higher baking temperatures at this step will tend to crack the resist because of the large coefficient of thermal expansion mismatch between PDMS and PMGI. Although the PMGI’s solvent system can swell PDMS, pattern fidelity is not affected by brief periods of solvent contact, like those experienced during typical spin coating processes. After softbaking, the sample was then exposed and developed to uncover the PDMS surface. See Fig. 2.

Carbon black filled PDMS was used as the compliant electrode material and prepared as follows. Three grams of PDMS base and 0.4 g cure agent (6.67 : 1 ratio) were fully dissolved in 15 mL xylenes. This solution was combined with 0.5 g carbon black and sonicated for 10 minutes. The solution was then further diluted six fold by volume with pure xylenes.

The PMGI/photoresist masking layer was then used to define the electrodes by airbrushing the carbon black/PDMS solution onto the wafer from approximately 10 cm away using short bursts. The airbrushed solution must be dilute and lightly applied otherwise the filled PDMS will conform to the sidewalls of the shadow mask, creating lift off complications. Once applied, the electrodes were cured at 65 °C for 1 hour in an oven inside a Petri dish. Cracking of the PMGI can occur over time if too much solvent is lost; however, the processing window lasts several hours, or potentially much longer if the specimen is kept in a solvent controlled atmosphere. During curing, excess silicon hydride groups in the electrode material bind covalently with the excess vinyl groups at the exposed PDMS interface, providing permanent adhesion between the two surfaces. PDMS bonding methods have been evaluated previously, clearly showing that layers with complimentary stoichiometry are superior and more consistent in strength relative to those based on oxygen plasma treatments. Lift off of the mask structure and simultaneous dissolution of the channel were carried out via immersion in 1165 photoresist stripper at 80 °C (Fig. 3). Sonication is not necessary to lift off the excess electrode material cleanly if the PMGI/imaging resist thickness is greater than twice the thickness of the airbrushed electrode material.

**Fig. 1** Peristaltic pump fabrication scheme. The photoresist (PR) is Novolak-based.

**Fig. 2** Optical micrograph of a PMGI shadow mask for defining electrodes on the PDMS surface. A fifty μm wide photoresist line encapsulated by PDMS forms the channel that carries fluid after resist dissolution/lift off.

**Fig. 3** Optical micrograph of compliant electrodes for the peristaltic pump after lift off of PMGI/photoresist.
The fabrication of 1- and 2-dimensional rectangular diffraction gratings is similar to that for the microfluidic pump (ESI†). Spin coating conditions differ from those for the pump fabrication in order to achieve thinner PMGI/photoresist layers but the methodology is essentially the same. Once the PMGI/photoresist is exposed and developed such that the grating is formed (Fig. 4), PDMS can be applied to encapsulate the structure fully. Freestanding and multilayer structures are also possible by applying a sacrificial layer of photoresist before the initial PDMS application and by repeating the PMGI processing after PDMS encapsulation, respectively (ESI†).

Contact angle measurements on PDMS indicate a significant difference in hysteresis between PMGI and its pure solvent system, T-thinner, implying surface adsorption of either polymer or surfactant molecules (Fig. 5).\textsuperscript{24} Although further investigation is necessary to confirm polymer adsorption, one salient feature of PMGI is that its molecular weight (\(M_w \approx 71 \text{ kDa}\))\textsuperscript{24} is above the critical threshold for entanglement (estimated \(M_c \approx 14.5 \text{ kDa}\)) (ESI†). We believe PMGI can form relatively stable films on PDMS because polymer chains in the bulk can entangle with polymeric species adsorbed on the PDMS surface. These entanglements may prevent perturbations from creating dewetting sites,\textsuperscript{25} and have been shown to substantially increase the film stability when adsorbed long chains are present.\textsuperscript{26} Although Novolak-based resists typically contain surfactants which may adsorb to PDMS, the polymer resins do not typically reach the entanglement limit\textsuperscript{27} and therefore tend to dewet on PDMS. SU-8 resin also has a low \(M_w (\sim 7 \text{ kDa})\) and is unlikely to entangle (ESI†).\textsuperscript{28}

Conclusions

A method of lithographically patterning on cured PDMS surfaces using PMGI has been presented. The entanglement of PMGI polymer with adsorbed polymer is suspected to aid film stability during spin coating on PDMS. The utility of this process can be applied in a multitude of ways to develop useful microfluidic or other micro- or nanoscale devices. The process for fabricating an electrostatically actuated microfluidic pump as well as diffraction gratings directly on PDMS has been outlined. Further characterization of the pump will be described in the future.

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