

Supplemental Information: Lithographic Patterning on Polydimethylsiloxane Surfaces using Polydimethylglutarimide

Materials

Novolak-based photoresists (Microposit S1813, Microposit S1805, Shipley; Megaposit SPR 220-7.0, Shipley), polydimethylglutarimide (PMGI) (PMGI SF-11, PMGI SF-15, MicroChem), solvent for PMGI (T-thinner, MicroChem), SU-8 2015 (MicroChem), developer for SPR 220-7.0 (CD-26, Shipley), photoresist stripper (1165, Shipley), polydimethylsiloxane (PDMS) (Sylgard 184, Dow Corning), carbon black (XC72R, Cabot), and xylenes (mixed isomers, VWR) were used as received. Developer for S1813 and PMGI SF series (AZ400K, Clariant) was diluted 1:4 with deionized water before use with PMGI/S1813. As or Sb doped Si wafers (0.001-0.005 ohm-cm prime grade (111), University Wafer) were cleaned in acetone, isopropanol and deionized water before being dehydrated at 115°C for >3 minutes. Hexamethyldisilazane (MicroPrime HP, ShinEtsu Microsi) was spin coated on the wafers prior to use for improved Si-PDMS adhesion.

Microfluidic Pump Fabrication

Channels

Photoresist (SPR 220 7.0) was spin coated on the cleaned and primed silicon wafer (500 rpm, 5s dispersal; 3000 rpm, 40s spin) and softbaked at 115°C for 3 minutes, then allowed to cool to room temperature in air. The resist was exposed to a dose of 840 mJ/cm² at 405nm through a chrome/quartz mask in a Karl Suss MJB-3 mask aligner. The sample was subsequently left alone for 5 minutes to allow completion of the photoreaction. CD-26 was used to develop the pattern with gentle pipetting for approximately 2.5 minutes until no further color changes were seen, before being rinsed in deionized water and blow dried with nitrogen. For additional stability of the channels, the resist was rounded on a hotplate at 120°C for 15 minutes. The resist reached a maximum height of 9.67 μm for a 120 μm wide channel as measured by stylus profilometry (3mg Dektak).

PDMS

The channels were then encapsulated in PDMS (15:1 base:cure agent by weight) which had been combined in a Thinky ARE-250 planetary mixer for at least 1 minute at 1600 rpm. PDMS was slowly applied to the sample after mixing; excess bubbles were removed with a pipet. The PDMS was spin coated (500 rpm, 5s dispersal; 3000 rpm, 60s spin) and degassed under house vacuum for 2 minutes before being cured in an oven at 65°C for 2 hours. The PDMS thickness was found to be 18.2 μm thick away from the channel after scraping a section of the PDMS away with a razor blade (stylus profilometry, 3mg Dektak).

PMGI

PMGI SF-11 was subsequently spin coated (500 rpm, 5s dispersal; 3500 rpm, 40s spin) on the cured PDMS surface. Without baking, S1813 imaging resist was applied via spin coating (500 rpm, 5s dispersal; 4500 rpm, 40s spin). The sample was then softbaked at 70°C on a hotplate for 2 minutes. The resist was exposed to a dose of 280 mJ/cm^2 at 405nm through a chrome/quartz mask. The sample was developed in AZ400K (1:4 dilution in deionized water) with gentle pipeting for 1 minute, then rinsed in deionized water and blow dried with nitrogen. The PMGI/S1813 features were found to be 10-10.5 μm (stylus profilometry, 3mg Dektak).

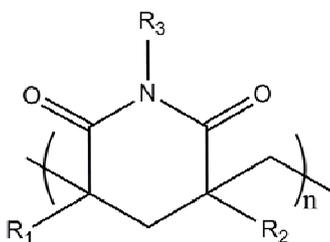


Figure 1: PMGI repeat unit. R groups are H, alkyl, aryl, alkaryl, or aralkyl groups, either substituted or unsubstituted.¹

Compliant electrodes

Three grams of PDMS base and 0.4g cure agent were fully dissolved in 15 mL xylenes. This solution was combined with 0.5g carbon black and sonicated for 10 minutes. The solution was then further diluted six fold by volume with pure xylenes. This solution was airbrushed (Paasche Airbrush, Co.) from approximately 10 cm away from the sample surface using short bursts, allowing the solution to dry between each application. Once the lithographically defined features were sufficiently dark and even in color, the sample was cured in an oven at 65°C for 1 hour in a petri dish. The excess electrode material was lifted off using 1165 at 80°C for 10 minutes, gently agitating with a pipet. Prior to immersion in 1165, the reservoirs on either side of the channel were opened using a razor blade so the SPR 220-7.0 channels could be dissolved along with the PMGI/S1813 features. Soaking in 1165 longer and rinsing with deionized water before reimmersion in fresh 1165 were helpful in removing residual SPR 220-7.0, especially for smaller channel cross sectional areas (<250 μm^2). The presence of residual photoresist can be detected by optical microscopy to determine if further 1165 immersion is necessary.

Diffraction gratings

PDMS (15:1 base:cure agent by weight), which had been mixed in a Thinky ARE-250 planetary mixer for at least 1 minute at 1600 rpm, was spin coated (500 rpm, 5s dispersal; 3000 rpm, 60s spin) onto a cleaned and primed silicon wafer and degassed under house vacuum for 2 minutes before being cured in an oven at 65°C for 2.75 hours. PMGI SF-11 was spin coated (500 rpm, 5s dispersal; 6000 rpm, 30s spin) on the PDMS without baking. S1813 was spin coated (500 rpm, 5s dispersal; 6000 rpm, 30s spin) on the PMGI and the sample was softbaked at 70°C for 2 minutes. The sample was exposed at 195 mJ/cm^2 through a quartz/chrome mask and developed for 15 seconds in AZ400K (20% aqueous) with gentle pipeting before being rinsed in deionized water and blow dried with nitrogen. The PMGI/S1813 features were found to have a thickness of 1.1 μm (stylus profilometry, 3mg Dektak). See Figure 2.

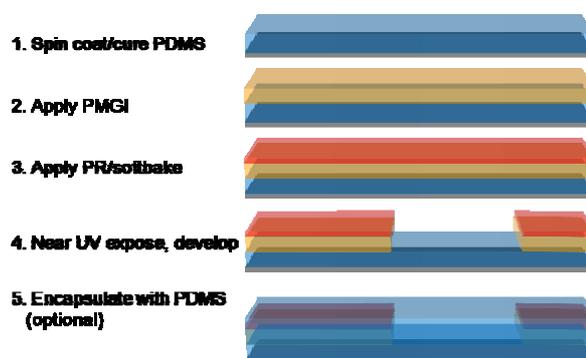


Figure 2: Processing sequence for producing diffraction gratings on PDMS surfaces.

Depending on the application, it may be advantageous to encapsulate completely the PMGI/S1813 pattern in PDMS. Mixed PDMS (6.67:1 base:cure agent by weight) is spin coated (500 rpm, 5s dispersal; 3000 rpm, 60s spin) on the PMGI/S1813 pattern and cured at 65°C in an oven for 2.5 hours. If desired, the PMGI/S1813 patterned structures can then be dissolved by creating an opening in the PDMS with a razor blade before the sample is immersed in 1165 at 80°C, similar to the process for compliant electrode lift off.

Freestanding and multilayer structures

Sacrificial layers of PMGI or other photoresists can be applied before the initial coating of PDMS to fabricate freestanding structures. For example, spin coating PMGI (500 rpm, 5s dispersal; 3000 rpm, 40s spin) on silicon and softbaking (190°C for 10 minutes to reflow and planarize), then letting the substrate cool in air to room temperature creates a sacrificial layer which can be spin coated with PDMS (15:1 base:cure agent by weight) (500 rpm, 5s dispersal; 3000 rpm, 60s spin) and cured at 65°C for 2-3 hours. Once the PDMS is cured, PMGI can be spin coated, patterned, and encapsulated with PDMS (6.67:1 base:cure agent by weight) as previously described for diffraction grating fabrication. Photoresist stripper (1165) can be used to release the encapsulated structure; it may also be useful to dissolve the encapsulated PMGI/S1813 structures at this stage by creating access with a razor blade. Multilayer structures are also

possible using this technique by repeating the PMGI patterning process on a PDMS-encapsulated PMGI/S1813 structure. Features with small cross sectional areas ($<250 \mu\text{m}^2$) may require rinsing the device in deionized water and reimmersion in photoresist stripper for complete resist removal. Optical microscopy can be used to verify qualitatively the presence of photoresist left in the channel as identified by reddish coloration.

Layer	Material	Diffraction grating application conditions	Diffraction grating layer thickness (μm)	Microfluidic pump application conditions	Microfluidic pump layer thickness (μm)	Baking ($^{\circ}\text{C}$, mins)	Exposure dose (at 405nm) (mJ/cm^2)	Photoresist development (chemical, duration (s))
Fluid channel (120 μm wide)	SPR-2207.0	N/A	N/A	500 rpm, 5s dispersal; 3000 rpm, 40s spin	9.67 (maximum)	Sulfbake, 115, 3; Rounding: 120, 15 (hotplate)	840	CD-26, 150
PDMS layer	Sylgard 184 (15:1 base:cureagent)	500 rpm, 5s dispersal; 3000 rpm, 60s spin	18.2	500 rpm, 5s dispersal; 3000 rpm, 60s spin	18.2	65, 120 (oven)	N/A	N/A
PMGI mask	PMGI SF-11	500 rpm, 5s dispersal; 6000 rpm, 30s spin	N/A	500 rpm, 5s dispersal; 3500 rpm, 40s spin	N/A	None	N/A	N/A
Imaging resist (Novolak) on PMGI	S1813	500 rpm, 5s dispersal; 6000 rpm, 30s spin	1.1 (PMGI + resist)	500 rpm, 5s dispersal; 4500 rpm, 40s spin	10 - 10.5 (PMGI + resist)	70, 2 (hotplate)	280 (pump) 195 (grating)	AZ400K (20% aqueous), 15 (grating)/60 (pump)
Compliant electrodes (500 μm wide)	Carbon black/PDMS (6.67:1 base:cure agent)/xylene	N/A	N/A	Airbrush	0.5 - 3	65, 60 (oven)	N/A	N/A

Figure 3: Chart summary of processing details. See text for clarification. Layer thicknesses were measured using stylus profilometry (3mg Dektak).

Critical Entanglement Molecular Weight Estimation

For random coil flexible polymers, $M_c \approx 30C_{\infty}M_0$ where M_c is the critical entanglement molecular weight, C_{∞} is the characteristic ratio, and M_0 is the repeat unit molecular weight.² Employing the equivalent freely jointed chain model, $\cos \theta$ is approximated with a Taylor series: $\cos \theta \approx 1 - \theta^2/2$ such that the following equation can be written:³

$$b/a = C_{\infty}/(\cos(\theta/2)) \approx 4/\theta^2$$

where b is the Kuhn segment length, a is the backbone bond vector length, θ is the supplementary angle to the smallest angle between backbone bond vectors. In the case of PMGI, $\theta \approx 60^\circ$, solving for C_∞ in terms of θ yields $C_\infty \approx 3.16$. Assuming that PMGI in Figure 1 possesses methyl groups for R1 and R2, and R3 is a hydrogen atom ($M_0=153\text{amu}$), $M_c \approx 30C_\infty M_0 = 30 \cdot 3.16 \cdot 153 = 14.504 \text{ kDa}$. Although these approximations can be low relative to experimentally determined C_∞ values, using a C_∞ of 10 (a reasonable upper bound for common polymers)³ yields 45.9 kDa, which is still lower than the PMGI M_w cited in example 1 of Gleim's patent (71 kDa).¹

Wetting Behavior

SU-8 2015 was spun cast (500rpm, 5s dispersal, 3000rpm, 60s) on a cured PDMS surface (15:1 base:cure agent by weight; 65°C cure, 2-3 hours) then annealed on a hotplate (65°C, 1 minute; 95°C, 2 minutes) to observe the surface coverage and wetting behavior. Although ~90% of the PDMS was covered with SU-8, upon annealing at 95°C, spontaneous dewetting was observed starting from the edges of the wafer and areas where air bubbles were left from spin coating. Where uniform, SU-8 was found to be ~36.7 μm thick (3mg Dektak). It should be noted that cyclopentanone, the major solvent of PMGI SF series, is also the major solvent for SU-8.

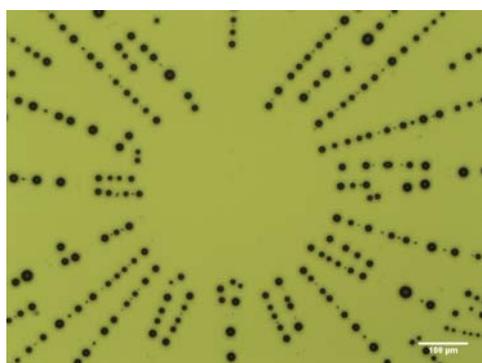


Figure 4: Optical micrograph of SU-8 dewetted on a PDMS surface after annealing. One hundred micron scale bar.

S1805 was spun cast (500rpm, 5s dispersal, 3000rpm, 40s) on a cured PDMS surface (15:1 base:cure agent by weight; 65°C cure, 2-3 hours) then annealed on a hotplate (115°C, 90s) to observe the surface coverage and wetting behavior. The resist incompletely covered the PDMS surface and seemed to dewet in several areas. No further dewetting seemed to occur during annealing. The resist was found to be ~5 μm thick where uniform (3mg Dektak).

Contact angle measurements were made on PDMS with a Ramé-Hart goniometer using a backlight and eyepiece crosshairs. 3-4 measurements were made for each data point shown in Technical Note Figure 5 and Figure 5 below. Measurement error comes from solvent evaporation/skin formation as well as not accounting for droplet volume or time of surface contact.

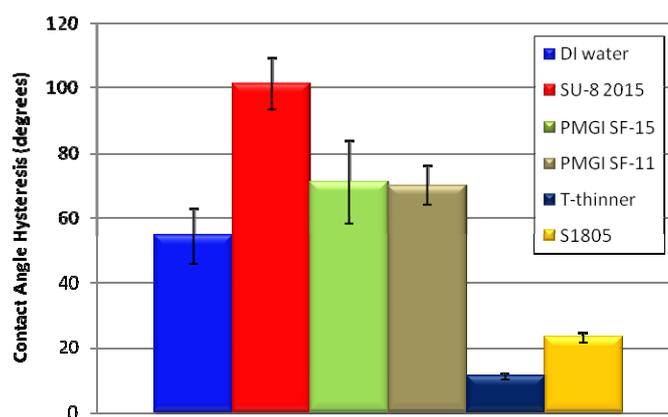


Figure 5: Contact angle hysteresis of various liquids on a cured PDMS surface. Hysteresis is the difference between advancing and receding droplet contact angle values. Standard error bars shown.

Johnson et al⁴ explains that for a polymer or surfactant solution, if a droplet produces different contact angle hysteresis values from that of pure liquids, it can be concluded that some type of specific interaction between the solute and the solid surface is occurring. Since PMGI SF series exhibits a significantly different hysteresis than its pure solvent (T-thinner) (Figure 5), either the PMGI polymer or its proprietary surfactant is having a specific interaction with the PDMS surface. Therefore, either PMGI polymer, its surfactant, or both are adhering to the PDMS surface. Yerushalmi-Rozen et al⁵ show that it

is essential to have a small amount of long chain (entangleable) adsorbed molecules to allow formation of stable films on a surface by a non-wetting polymer solution. Without these adsorbed chains on the surface, even if the polymer in solution is far above the critical entanglement weight, the polymer solution will tend to dewet. Spangler et al⁶ describes how entanglement (or high viscosity) impedes the flow of solution, reducing the film's susceptibility to wave perturbations. Although we do not know at this time whether it is polymer or surfactant adsorbing to the PDMS or in what ratio, given the possibility for PMGI hydrogen bonding to PDMS, we hypothesize that some long polymer chains are adsorbing to the PDMS surface. We have identified that SU-8 does not form stable films on PDMS (Figure 4); in agreement with our entanglement argument, SU-8's molecular weight ($7\pm 1\text{kDa}$)⁷ is below the critical entanglement limit (low end M_c estimate, $C_\infty=5$, $M_w=338\text{amu}$: $M_c:50.7\text{kDa}$), making it susceptible to perturbations which prevent the formation of a stable layer. The same principle should hold for Novolak resins such as S1805 as their molecular weight is known to be below the critical entanglement threshold.⁸

We believe that PMGI polymer chains are adsorbing on the PDMS surface and entangling with PMGI chains in the bulk during spin coating, creating a stable film. We believe that PMGI exhibits this entanglement in contrast to most photoresists, including SU-8 and S1805, leading to its relative stability on PDMS. Further investigation of PMGI's stability on PDMS is still needed for verification of this hypothesis.

References

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