Supplementary Information

Multi-functional Silicone Stamps for Reactive Release Agent Transfer in UV Roll-to-Roll Nanoimprinting

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Master preparation: Large area nickel and silicon master molds were fabricated using conventional top-down photolithography and nickel electroforming techniques. The precise dimensions of all molds employed are provided in Table S1. These masters were hydroxylated via oxygen plasma treatment for 2 minutes, followed by vapor deposition of 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (FDTS) under vacuum at 120 °C for 2 hours in order to form a SAM anti-stick coating on the patterned master surface. The molds were then thoroughly cleaned with IPA to remove loose FDTS chains, dried by nitrogen gas gun and baked at 180 °C for 2 hours.

Table S1. Feature geometries, tolerances and material composition of master molds used for h-PDMS/PDMS roll-mounted stamp replication.

	Feature Diameter (Linewidth) (nm)	Feature Height (nm)	Feature Pitch (nm)	Tolerance (± %)	Material
500 nm diameter, AR 1 hole mold (pillar imprint)	500	500	1000	10	Electroformed Nickel
500 nm linewidth, AR 4 grating mold	500	2000	1000	10	Silicon

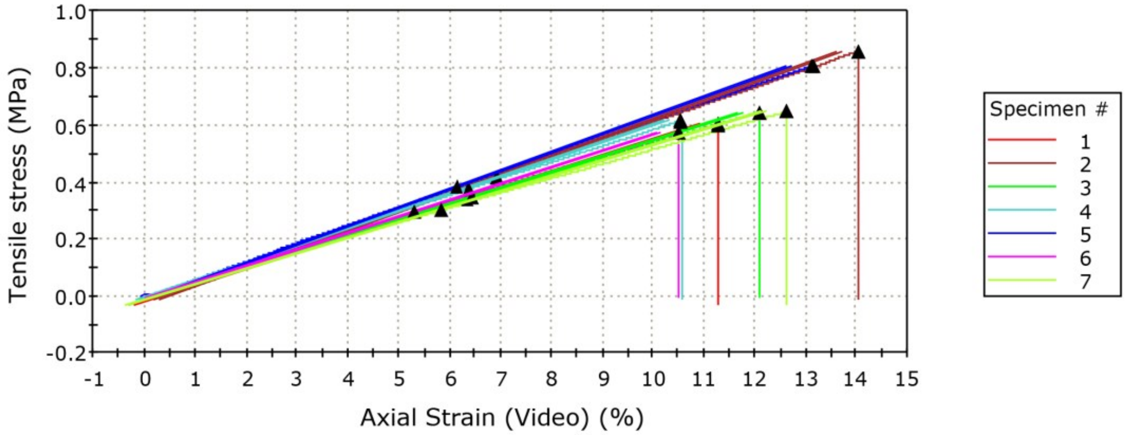
Fabrication of h-PDMS / PDMS stamps: h-PDMS was prepared from VDT-731 (Gelest) vinyl PDMS prepolymer, HMS-301 (Gelest) hydrosilane crosslinker, platinum divinyltetramethyldisiloxane catalyst (SIP6831.2LC, Gelest) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane modulator (87927, Sigma-Aldrich). The fabrication process follows a similar format to that detailed in Odom et al.,[1] but with modifications to the prepolymer formulation. First, the HMS-301 crosslinker weight fraction was reduced from 22.6 to 20.6% wt., while the 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane inhibitor fraction was increased from 0.4 to 2% wt. This was done because h-PDMS prepared according to the literature formulation is very brittle and fails easily by cracking across the stamp face during separation from the master, tensioned mounting onto a roll cylinder, or from the imposition of swelling mismatch stresses upon absorption of liquids, especially for large area h-PDMS/PDMS stamps. The reformulated h-PDMS exhibited significantly improved scalability and pot life at the expense of modulus. The resulting h-PDMS in its cured state obtained a bulk modulus of ~6 MPa, still approximately three-fold greater than Sylgard 184 PDMS and with significantly improved resistance to cracking at large area (Figure S1).

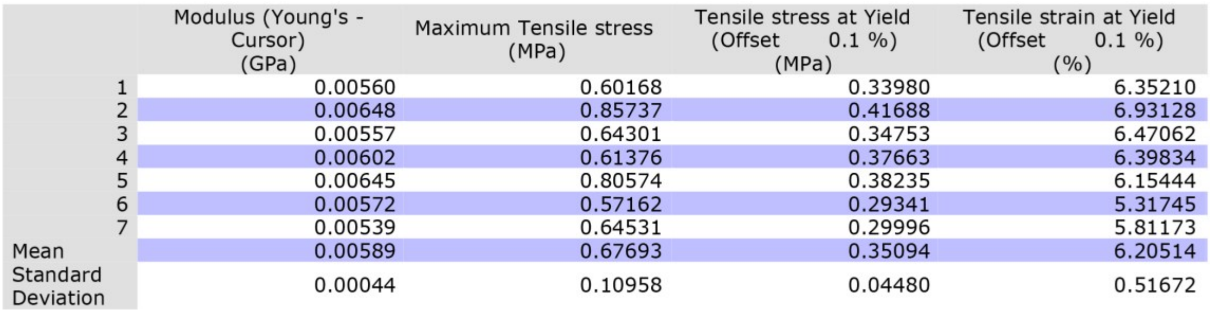
Table S2 shows concisely the compositional changes relative to the literature. 3.7 g of VDT-731, 50 μL of platinum catalyst and 0.05 g of modulator were thoroughly mixed and degassed under vacuum for 10 minutes. 1 g of HMS-301 was then added and mixed thoroughly for 10 minutes and vacuum degassed for 5 minutes. Prior to spincoating the h-PDMS prepolymer, toluene was dispensed onto the spinning master mold in order to facilitate wetting and filling of mold features with h-PDMS.[2] Immediately after spin drying, h-PDMS was coated onto the master mold at 6000 RPM for 30 seconds, forming an ~10 μm thick h-PDMS film. The h-PDMS coated masters were then allowed to stand at room temperature for two hours to gel instead of baking at elevated temperature (as in the literature). Sylgard 184 (Dow Corning) was then poured on top of the gelled h-PDMS films (~2 - 3 mm thick layer) and cured overnight at 60 °C. After curing, the h-PDMS/PDMS composite stamps were carefully trimmed and peel separated from the master. For grating stamps, the peel separation direction was always oriented parallel to the grating lines.

Table S2. h-PDMS formulation from literature with comparison to the modified formulation for large area roll-mountable h-PDMS/PDMS stamps used in the present work.

	VDT-731 (g)	Platinum divinyltetramethyl disiloxane catalyst (uL)	2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-cyclotetrasiloxane inhibitor (g)	HMS-301 (g)	Young's Modulus (MPa)
Schmid, Odom et al.[1, 3]	3.4	18	One drop (~0.01 – 0.02)	1	Up to 9 MPa
Modified Formulation	3.7 (76.3% wt.)	50 (~1% wt.)	0.1 (2% wt.)	1 (20.6% wt.)	~6 Mpa SD ±0.4

Tensile mechanical testing of reformulated h-PDMS: was carried out on h-PDMS strips that were punched from flat, featureless h-PDMS sheets produced using the modified h-PDMS formulation provided in Table S2 for the purpose of determining the modulus. An Instron 5569 Universal Testing System with pneumatic side-action grips was used to apply a progressive tensile load to 20 x 5 x 0.53 mm thick strips for the purposes of determining the modulus. The tensile load was measured with a 10 N load cell. The strain was measured using a non-contact video extensometer at an extension rate of 1 min^{-1}, giving a strain rate of 0.05 min^{-1}. The mean tensile modulus of this formulation was found to be ~6 MPa measured across 7 specimens (Figure S1). Alternatively, where the axial strain at failure is taken as a figure of merit denoting a sample with more uniform mixing and lower defectivity, then the modulus of the sample with the largest axial strain at failure given as ~6.5 MPa can also be taken as a reasonable measure. This compares to ~1.8 MPa for Sylgard 184 PDMS and ~9 MPa for h-PDMS as provided in the literature.[3, 4]





	Modulus (Young's - Cursor) (GPa)	Maximum Tensile stress (MPa)	Tensile stress at Yield (Offset 0.1 %) (MPa)	Tensile strain at Yield (Offset 0.1 %) (%)
1	0.00560	0.60168	0.33980	6.35210
2	0.00648	0.85737	0.41688	6.93128
3	0.00557	0.64301	0.34753	6.47062
4	0.00602	0.61376	0.37663	6.39834
5	0.00645	0.80574	0.38235	6.15444
6	0.00572	0.57162	0.29341	5.31745
7	0.00539	0.64531	0.29996	5.81173
Mean	0.00589	0.67693	0.35094	6.20514
Standard Deviation	0.00044	0.10958	0.04480	0.51672

Figure S1. Stress-strain plot for the modified h-PDMS formulation, measured across seven 20 x 5 x 0.53 mm h-PDMS strips. Mean Young's Modulus was measured to be ~6 MPa, while the sample with the largest axial strain obtained a Modulus of ~6.5 MPa.

h-PDMS treated glass: h-PDMS pre-polymer (as above) was spincoated onto supported 100 mm x 100 mm x 0.1 mm flexible glass sheets at 2000 RPM for 30 seconds and allowed to stand for 1 hour prior to complete removal with hexanes in an ultrasonic bath. The clean, treated glass sheets were then baked in an oven overnight at 60 °C.

mPDMS release agent exposure: Asymmetric monomethacryloxypropyl-terminated polydimethylsiloxane (mPDMS, MW 600-800, 6-9 mPa·s, Gelest MCR-M07) was pooled into a clean petri dish or other flat-bottom container and the h-PDMS/PDMS stamp (or h-PDMS treated glass) was laid with the h-PDMS patterned face down into mPDMS for 3 minutes such that only the patterned face is immersed in mPDMS. After removal, excess mPDMS is thoroughly removed using a nitrogen gas gun.

Acrylate resin formulation: A test bed acrylate resin formulation comprised of 59% wt. 1,6 hexanediol diacrylate monomer, 39% wt. neopentyl glycol diacrylate crosslinker, and 2% wt. 4,4'-bis(diethylamino)benzophenone photoinitiator was formulated in an amber vial. The formulation was agitated for 2 hours to thoroughly mix all components, and bubbled with nitrogen for 2 hours to remove oxygen. Solubility with mPDMS was confirmed by loading the above resin formulation to various concentrations up to 8% wt., followed by agitation for 2 hours. All solutions remained visibly clear to the naked eye, with phase segregation occurring upon polymerization as a coating at mPDMS concentrations above 4% wt.

Resin mold fabrication via UV roll-to-roll nanoimprinting: Fabricated h-PDMS/PDMS stamps with embedded mPDMS were wrap mounted by mechanical fixation to the imprint roller of our lab-scale UV roll-to-roll nanoimprinting system (SRS 400, Solves Innovative Technology). 125 μm thick, 300 mm wide and 100 m long polycarbonate reels with double-sided protective covering layers were used as the substrate web material. During the roll-to-roll nanoimprinting process, the test bed acrylate resin is deposited directly onto the h-PDMS/PDMS stamp via inkjet dispense following a pre-programmed drop map. Spreading of the resin drop field into a coating on the polycarbonate web is obtained via soft rubber spreading rollers, followed by high intensity 395 nm UV LED exposure (peak irradiance of 8 W cm^{-2} at the array emitting window) at 1 meter min^{-1} to ensure complete curing. This will cure the resin coating against the h-PDMS/PDMS stamp with embedded mPDMS, allowing transfer of surface mPDMS to the newly fabricated resin mold. Finally, the resin mold is peel separated from the h-PDMS/PDMS stamp as the polycarbonate web line is drawn away from the imprint drum. Blank resin molds prepared for contact angle goniometry and XPS analysis were prepared in the same manner as above using blank h-PDMS/PDMS sheets with embedded mPDMS, or h-PDMS treated flexible glass with physisorbed mPDMS.

Blank resin mold preparation for contact angle goniometry: Blank, reference acrylate resin molds were fabricated against polished flat, silicon-free nickel shims without any surface modification in our UV roll-to-roll nanoimprinting apparatus as above. Pure mPDMS films were prepared via spincoating on silicon wafer chips at 5000 RPM for 30 seconds followed by immediate self-polymerization under low pressure mercury arc lamp (254 nm) exposure in an inert nitrogen environment for 1 hour.[5, 6] Sylgard 184 PDMS films were prepared by casting a 10:1 degassed mixture of prepolymer base and hardener, respectively, against square silicon wafer chips, followed by curing overnight in an oven at 60 °C. The PDMS squares were then peeled off the silicon chips and trimmed.

Extraction of h-PDMS / PDMS Sheets for contact angle and XPS analysis: In order to extract native, unreacted oligomeric silicone chains, h-PDMS/PDMS sheets were immersed in sequential baths of 2-propanol, acetone and ethyl alcohol for 24 hours each following in order of descending swelling ratio. Other solvents were attempted, however those that were known to have a PDMS swelling ratio $\gtrsim 1.1$ failed due to cracking. All baths were left at room temperature and agitated with a stir bar. The bath sequence was repeated twice, such that the extraction process lasted for 6 days. Following the final bath immersion, the h-PDMS/PDMS sheets were dried under vacuum overnight and were then exposed to mPDMS release agent as laid out in the Experimental section. Following this, a reference XPS scan of the first cured blank resin mold (resin formulation provided in the Experimental Section) produced from a pristine, extracted h-PDMS/PDMS sheet produced a silicon (Si2p) surface concentration of only 0.76%.

This compares to 7.19% for the first blank resin mold produced from a post-mPDMS treated h-PDMS / PDMS sheet from the 20 sample series shown in Figure 4 of the main text.

Contact angle measurement procedure: Contact angle measurements were acquired with a Rame-Hart Contact Angle Goniometer (NRL 100) using the sessile drop method. Two probe liquids, DI water and diiodomethane were used. Our instrument deposits the sessile drop from a dispense tip located just above the sample surface. Drop placement was carried out while the holding plate was level and care was taken to ensure that the drop contact line was reproducibly circular and that the drop contact area with the blank resin mold surface was approximately reproducible between drops and between test liquids prior to commencing the experiment. Drop volumes were set at 10 μL for DI water and 3 μL for diiodomethane to approximately match the drop contact area between test liquids and also to obtain a relatively large sampling area without exceeding the capillary length for the test liquids (i.e. a circular drop contact radius of 2.7 mm for DI water and 2.3 mm for diiodomethane). Profile images of drops were taken using a CCD camera at 640 x 480 pixels while backlit with a diffused halogen lamp. Contact angle measurement and image capture was accomplished manually immediately after drop deposition (approximately within 5 seconds of deposition). For each sample, five different locations on the surface were measured.

X-Ray photoelectron spectroscopy (XPS) measurement procedure: XPS characterization of cured blank resin molds was carried out with a VG ESCALAB 220i-XL ultra-high vacuum system. Blank (featureless) resin molds were used for this analysis because the spot size of the x-ray beam can be no smaller than 150 μm, and structuring the resin mold with features of diameter below this value would affect how electrons scatter off the surface and contaminate the data. These blank resin molds were produced using exactly the same process (as above) as those that were produced with a pattern. There should be no difference in behaviour between blank and structured resin molds in terms of whether or not mPDMS release agent will sustainably transfer to either surface and the overall trends in the data, as the only physical difference is an increase in the interfacial area due to structuring. Changes to the interfacial area should only vary the absolute amount of release agent transfer.

The XPS instrument was equipped with a monochromatic Al Kα (1486.6 eV) source and a concentric hemispherical energy analyzer. The analysis chamber pressure was ~10^{-10} Torr. Data was collected in the form of survey scans and high energy resolution scans of carbon 1s, oxygen 1s and silicon 2p peaks. Survey and high energy resolution scans were collected with pass energy of 150 eV and 10 eV, respectively. The presence and amplitude of the silicon 2p peak at 102 eV, which is associated with silicon in the dimethylsiloxane bonding configuration, was used to indicate the presence and relative surface concentration of transferred mPDMS silicon-containing oligomers on resin mold surfaces from the h-PDMS/PDMS sheet or h-PDMS treated glass, as the case may be. Peak data from carbon, oxygen and silicon were converted in Thermo Scientific Avantage software to relative surface atomic concentrations for each sample.

Sample preparation for SEM cross-section analysis: Silicon master mold, pristine h-PDMS/PDMS stamp, and resin mold samples comprising of 500 nm linewidth, aspect ratio 4, 1:1 duty cycle gratings (Table S1) were sectioned perpendicular to the direction of the grating. For the resin mold samples, liquid nitrogen was used to induce brittle failure upon sectioning. After coating with platinum, samples were mounted vertically on an SEM stub and loaded into a JEOL JSM-7600F FEG-SEM instrument. The cross-section was then tilted to be in-plane with the scan window for image capture and dimensional measurement.**Comparison of feature swelling to bulk swelling ratio:** It is important to note that the degree of swelling due to mPDMS absorption is dynamic and varies with the duration of contact with liquid acrylate resin in the UV roll-to-roll nanoimprinting process. Contact with the resin sets up a sharp mPDMS concentration gradient at the h-PDMS / resin interface and a consequent diffusive flux of mPDMS into the resin. This will tend to de-swell the h-PDMS features. Since a low viscosity, low molecular weight acrylate resin formulation was used to ensure compatibility with the inkjet dispensing strategy employed by our UV roll-to-roll nanoimprinting system, non-polar components of the resin are also absorbed by the h-PDMS / PDMS stamp. Thus there is a fluid exchange that occurs upon contact with the acrylate resin as evidenced by bulk swelling measurements plotted in Figure S2. Equilibrium swelling measurements of 30 x 30 x 5 mm sheets of solid h-PDMS immersed in liquid mPDMS and our formulated acrylate resin were recorded over 6 days using a microbalance to obtain the mass of the swollen network. The swelling ratio was calculated from the well-known formula:[7]

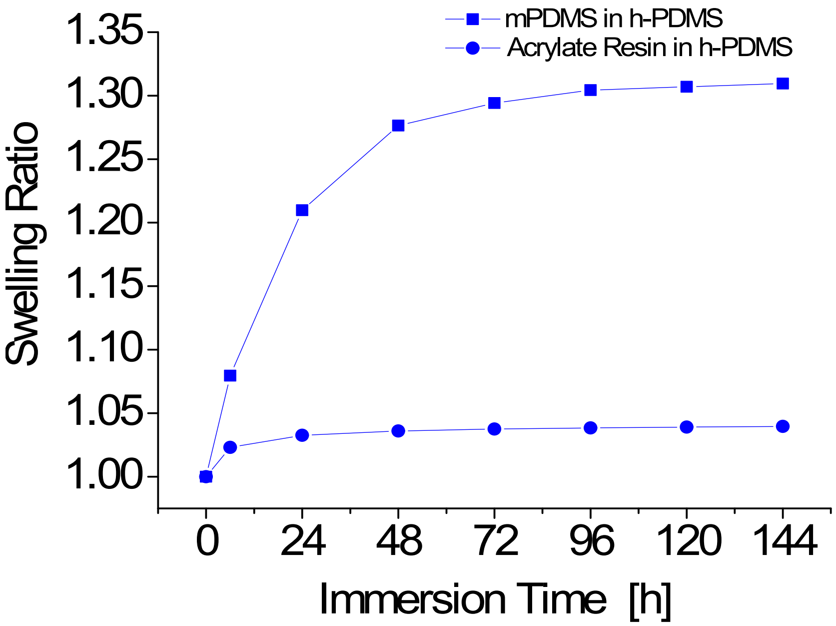
$$S = 1 + \frac{M_f - M_o}{M_o}\left(\frac{\rho_N}{\rho_s}\right) \tag{S1}$$

where S is the swelling ratio, M_o is the dry weight of the polymer network and M_f is the swollen mass (of the network and solvent combined). Figure S2 shows the evolution of the h-PDMS swelling ratio over time for mPDMS and acrylate resin solvents, and shows that both liquids will dissolve in an h-PDMS/PDMS mold in addition to being miscible in each other. Thus, when an mPDMS embedded h-PDMS / PDMS stamp is brought in contact with liquid resin, the h-PDMS stamp features will tend to de-swell as the fluid exchange takes place as has been shown for other de-swelling solvent combinations.[8] Note here that the h-PDMS sheets were not solvent extracted prior to immersion in mPDMS as doing so would be inconsistent with the history of h-PDMS / PDMS stamps prepared specifically for resin mold fabrication in the present study.

To show that the results presented in Figure 5c and Table 2 in the main text are minimally affected by the de-swelling effect induced by contact with the resin, Table 2 linear dimensional swelling values were converted to an effective swelling ratio of 1.25 – 1.26, which is close to the Figure S2 equilibrium bulk value of 1.31 after 6 days. The Table 2 linear change in line width and change in line height feature measurements of resin molds with respect to the Si master mold were converted to volumetric results according to the equation

$$V = 3L - 3L^2 + L^3 \tag{S2}$$

where V is the decimal volumetric change and L is the decimal linear change. The residual difference in swelling ratios can be attributed to losses to the resin coating as well as the fact that the bulk swelling



measurement is at equilibrium, whereas the calculated value from Table 2 is a surface measurement after a 3 minute exposure to mPDMS. In the latter case, the surface structures are able to quickly swell to near-equilibrium as the mPDMS diffuses from the surface of the sheet inwards toward the center.

Figure S2. Plot showing the evolution of the swelling ratio (dimensionless) for 30 x 30 x 5 mm sheets of solid h-PDMS in liquid mPDMS (squares) and acrylate resin (circles) solvents over a period of 6 days. Connecting lines are intended to guide the eye.

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