Supporting information for

Spatially Selective and Density-Controlled Activation of Interfacial Mechanophores

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1. MATERIALS

Polished silicon wafers, Si(100) with 300 nm thermal oxide layer, were purchased from University Wafers Inc. (Boston, MA, U.S.A.) for sample fabrication. Dimethyl sulfoxide (DMSO) (≥99.9%) was purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.) and used without further purification. Ethanol (200 proof) was purchased from Sigma Aldrich. Water (≥18.2 MΩ) was purified by a Milli-Q system (Q-GARD 2, Millipore, Billerica, MA, U.S.A.). Polished silicon wafers, Si(111) doped with boron, were purchased from Virginia Semi-conductor Inc. (Fredericksburg, VA, U.S.A.) and used for cantilever calibration. Sulfuric acid (95.0%), hydrogen peroxide (30% aqueous solution) were purchased from Sigma-Aldritch (St. Louis, MO, U.S.A.). Nitrogen gas (99.999%) was purchased from Praxair, Inc. (Danbury, CT, U.S.A.). AC240TS-R3 silicon cantilevers were purchased from Oxford Instruments Asylum Research (6310 Hollister Ave, Santa Barbara, CA, 93117, U.S.A.). All other materials were used without further treatment or modification, unless otherwise stated.

2. CONFIRMATION OF MECHANOCHEMICAL ACTIVATION USING FLUORESCENCE MICROSCOPY, TOF-SIMS, OPTICAL MICROSCOPY, AND AFM TOPOGRAPHIC IMAGING

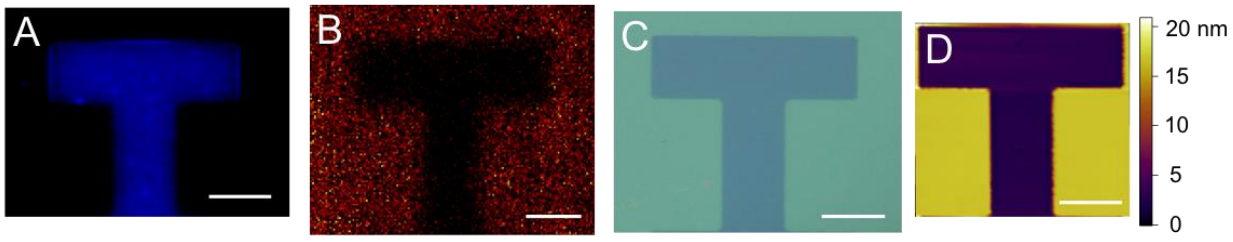

Figure S1. Confirmation of interfacial mechanophore activation using AFM lithography. (A) Fluorescence image of an 'T' feature fabricated. (B) ToF-SIMS image for fragment 41.99 u (CNO^-) which corresponds to the maleimide moiety of the fabricated 'T' feature. (C) Optical image of fabricated the 'T' feature. (D) AFM topographic image of fabricated 'T' feature. The scale bars are 20 μm.

Chemical and topographical changes after mechanochemical activation of interfacial MA at micrometer scale were confirmed with fluorescence microscopy, Time of Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS), optical microscopy, and AFM. Shown in Figure S1A, the fluorescence image was collected from 410-430 nm emission upon 360 nm excitation, which detects fluorescence from the surface bound anthracene.[1]The fluorescence signal exclusively from the fabricated region confirms that high contact force successfully translated to mechanochemical activation. ToF-SIMS (Figure S1B) for the CNO^- negative ion, originating from the maleimide fragment,[2] was collected to map surface distribution of the intact MA adduct on the surface after fabrication. A low concentration of maleimide moiety was detected inside the fabricated 'T' feature, whereas the intact regions showed a relatively high concentration. This result is consistent with the fluorescence measurements that showed selective mechanophore activation where high contact force was applied, which led to the loss of the maleimide fragment. The optical micrograph in Figure S1C shows color contrast between the fabricated region and intact region due to removal of the polymer brush. AFM topography image shows height difference after fabricating the 'T' feature with 450 nN contact force, which further verifies the

removal of the PGMA brush. Details of each experiment are provided below and in the main text.

3. CONTROL SAMPLES

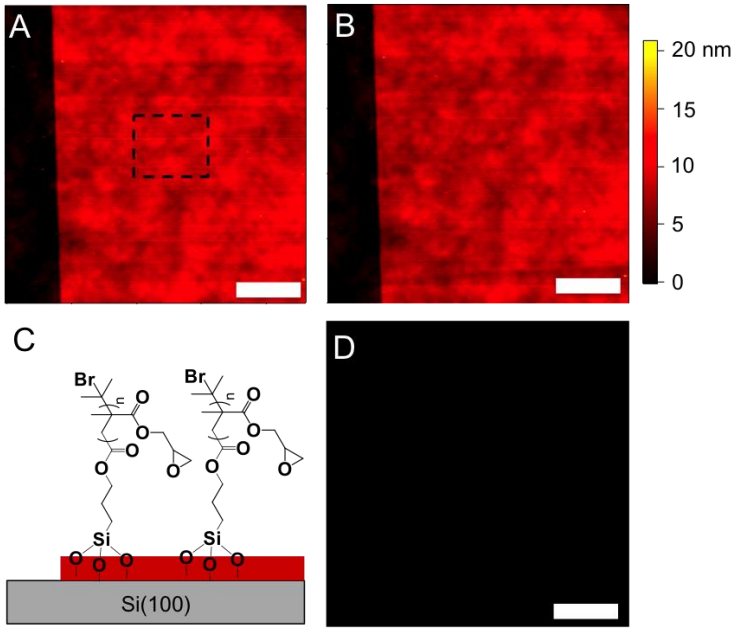

Figure S2. Images (A) and (B) were acquired under identical conditions as Figures 2A and 2B, respectively, except that the surface adsorbates were polymer brushes without mechanophores. (C) Schematic diagram illustrates the surface functionalities corresponding to the AFM image S2B. (D) Fluorescence image of the same region as B. All scale bars are 5.0 μm.

To determine if PGMA removal was due to the mechanophore group, and to verify that the PGMA brush itself is stable under high force, we subjected a control sample (see Figure S2C) to the same 450 nN force with identical scan parameters as the mechanophore sample shown in Figure 2. The control sample shows no height decrease after high force application (see Figure S2B), indicating none of the PGMA brushes were cleaved. Upon 360 nm excitation, the control sample showed no detectable fluorescence at 410-430 nm (Figure S2D), further verifying that the fluorescence seen in the mechanophore sample is due to the cleavage of the maleimide-anthracene moiety.

4. PRODUCTION OF HIERARCHICAL PATTERNS

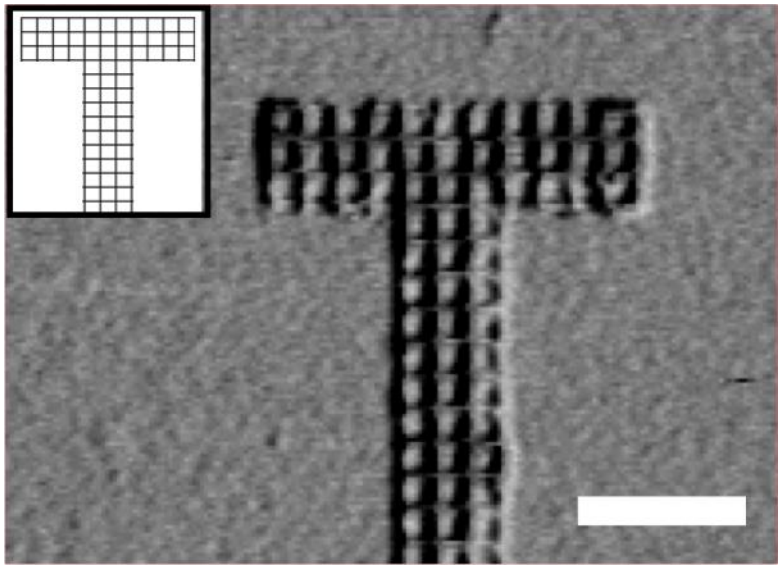

Figure S3. Example of hierarchical feature produced using AFM. The lateral AFM image of the hierarchical feature is shown. (Inset) An 'T' feature patterned with a square grid, custom designed. The scale bar is 1.0 μm.

The robustness of the spatially selective activation was further demonstrated by producing a hierarchical feature (Figure S3). Using the design tool included in the AFM's software (MicroAngelo macro written using Igor Pro 6.34), the hierarchical structure was designed in two steps: first, the hollow letter 'T'; second, periodical squares fill the space within the hollow 'T' feature. Upon setting the load (700 nN) and the physical dimensions, the AFM scan replicated the design in a couple of minutes. In the lateral force image shown above, the anthracene-termini region exhibited lower friction than surrounding polymer brush terminated by tert-butyl bromide, which is expected given the hydrophobic nature of the anthracene termini and the hydrophilic character of the cantilever. The grids lines of the 'T' feature were 83 nm wide. The inner grid rectangles measured 142 nm x 161 nm, while the size of the overall feature is 2.2 μm x 2.8 μm. This magnitude of difference in size indicates that this method is capable of producing small features without sacrificing the fidelity of the larger scale feature, verifying its robustness. The

fidelity of the feature produced coupled with the magnitude in difference in feature size verifies the robustness of the high activation of the MA mechanophore using AFM technology.

5. SAMPLE FABRICATION PROCESS

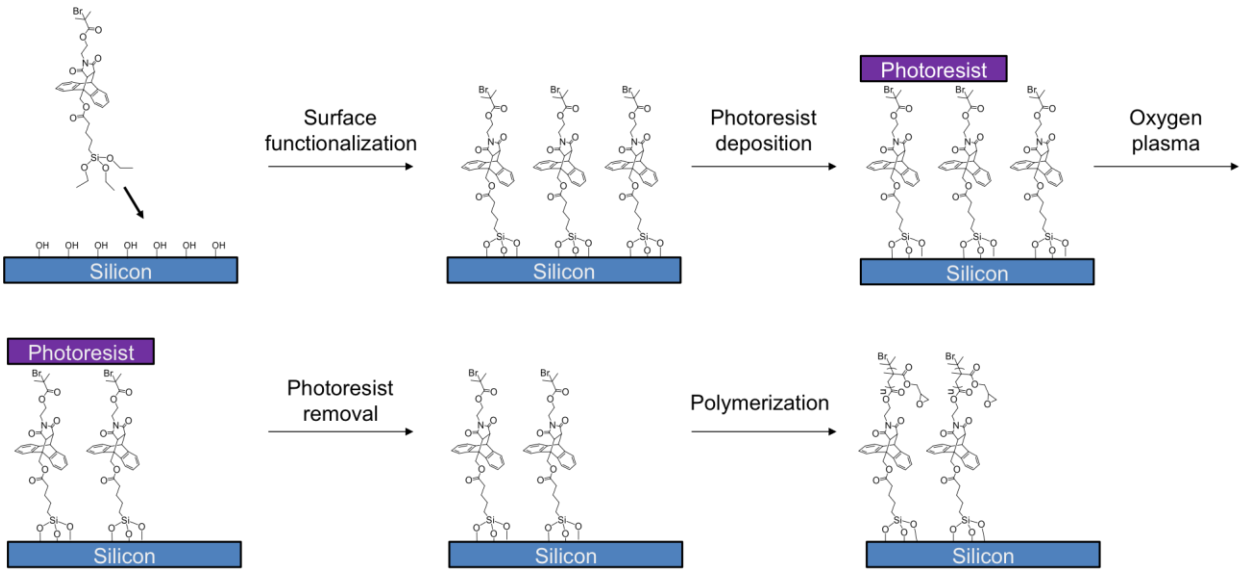

Figure S4. Fabrication steps for patterned PGMA brush-MA mechanophore grafted active specimen on silicon substrate.

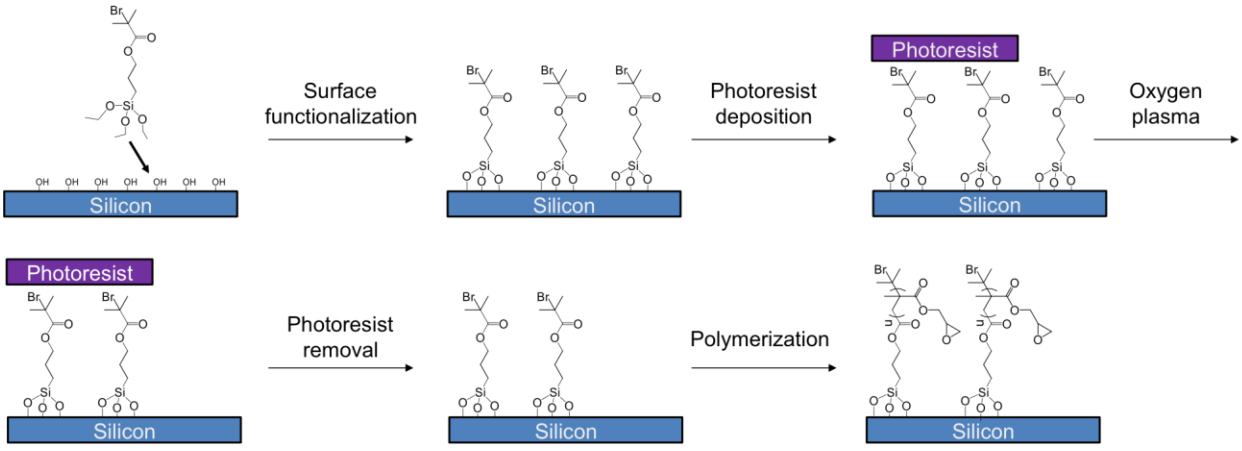

Figure S5. Fabrication steps for patterned PGMA brush grafted control specimen on silicon substrate.

5.1 Active Specimen Fabrication

Active specimens with Maleimide-Anthracene (MA) mechanophores immobilized on the surface were prepared with a surface functionalization approach following previously reported methods, shown in Figure S4.[3] In this work, the surface-bound MA mechanophores terminated with a bromoisobutyrate group were used to initiate a copper-catalyzed living radical polymerization of glycidyl methacrylate to grow polymer brushes.

5.1.1 Surface Functionalization of Silicon Substrate with MA Mechanophore

500 μm thick silicon substrates with 300 nm thermally grown oxide layer were cleaned in piranha solution at 120 ℃ for 30 minutes. Cleaned substrates were washed with DI water and dried in a stream of air. The substrates were further dried in a convection oven at 120 °C for 30 minutes. For surface functionalization, cleaned substrates were immersed in a 10 mM toluene solution of functionalized maleimide-anthracene adduct and kept in a sealed container for 24 hours on a bench top. After 24 hours, the substrates were sonicated in toluene and subsequently rinsed with toluene, isopropyl alcohol, and DI water followed by drying under a stream of air.

5.1.2 Surface Patterning MA Mechanophore Functionalized Silicon Substrate

The patterned MA surface was fabricated by photo patterning a photoresist (AZ 5214 E, microChem) and removing exposed MA moieties with oxygen plasma (Harric Plasma Cleaner Pdc-32g)[4]. After oxygen plasma treatment, residual photoresist was removed by rinsing with N-methyl-2-pyrrolidone.

5.1.3 Polymer Brush Formation on MA Functionalized Substrate

Poly(glycidyl methacrylate) brushes with varying thicknesses were synthesized on MA initiator-functionalized substrates using ARGET-ATRP.[5] Silicon substrates with patterned MA

initiator were placed in 20 ml vial containing 2 ml methanol/DMF/anisole (1:1:1 volume ratio). To the vial, 1.7 g of glycidyl methacrylate (Sigma-Aldrich, filtered through basic alumina to remove inhibitor) and 2 ml of a catalyst stock solution (containing 0.0036 mmol $CuBr_2$ and 0.036 mmol PMDETA) were added. After mixing, the vial was purged with nitrogen for 20 minutes. Ethyl-2-bromoisobutyrate (7 μl, EIB) was added to simultaneously initiate solution polymerization of glycidyl methacrylate along with the surface-initiated polymerization. The molecular weight of free polymer EIB-PGMA was used as a reference to estimate the degree of polymerization of the surface attached polymer.[6] The mixed solution was subjected to three cycles of freeze-pump-thaw process for complete degassing. After degassing, vial was filled with nitrogen and 1 ml ascorbic acid stock solution (8.4 mM ascorbic acid in methanol/DMF/anisole (1:1:1 volume ratio) solvent) was added. Four samples were prepared, which were polymerized for 10 minutes (three samples) and 20 minutes (one sample). After polymerization, the specimen was washed with DCM and ethanol. To remove residual solvent, we dried the silicon substrate in a vacuum oven at 50 ℃ for 24 hours. Representative size exclusion chromatography data is shown in Figure S6. The weight average molecular weight (M_w), number average molecular weight (M_n), and PDI of the synthesized polymer is summarized in Table S1. Thickness of the polymer brush was determined using AFM probe in DMSO, which were 11.4 ± 1.2 and 26.0 ± 1.3 nm. For the sample containing the gradient feature, spiral pattern, and the hierarchical 'T' pattern, the exposed silicon surface after oxygen plasma etching was functionalized in 10 mM 2-[methoxy(polyethyleneoxy)6-9propyl]trichlorosilane(oligomeric ethylene oxide) (Gelest) toluene solution. For the samples with the passivated oligomeric ethylene oxide surfaces, the polymer brush heights were 9.2 ± 0.6 and 10.7 ± 1.3 nm relative to the surrounding oligomeric ethylene oxide. The oligomeric ethylene oxide layer height was measured at 1.4 ± 0.2 nm.

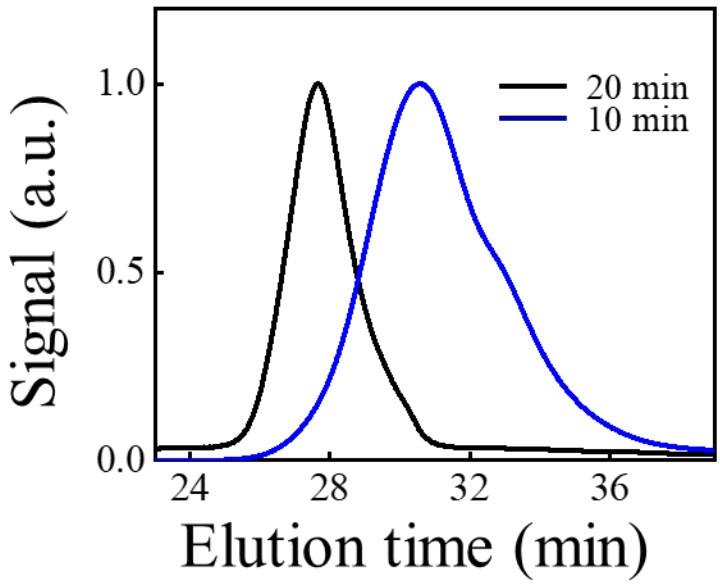

Figure S6. Representative size exclusion chromatography results of the synthesized PGMA for the 10 and 20 min polymerization times.

Table S1. The Weight Average Molecular Weight (M_w), Number Average Molecular Weight (M_n), and PDI of the Synthesized PGMA for 5, 10, 20 min Polymerization Time

Specimen	Figures 2, 4, 5	Figure 3
Polymerization Time	10 min	20 min
M_w (kDa)	29.1	46.9
M_n (kDa)	22.2	40.8
PDI	1.31	1.15
Brush Height	11.4 ± 1.2 nm, 10.6 ± 0.6 nm, 12.1 ± 1.3 nm	26.0 ± 1.3

5.2 Control Specimen Fabrications

The control specimen (Figure S5) was fabricated to investigate the effects of high-load force on PGMA brush without the MA mechanophore. The control specimen was prepared using a similar fabrication steps to that of the active specimen. Piranha-cleaned silicon substrate was functionalized with (3-(trimethoxysilyl)propyl 2-bromo-2-methylpropionate, Gelest) by immersing it in 10 mM toluene solution for 24 hours. The functionalized surface was subsequently patterned using photolithography. PGMA brush was prepared by ARGET-ATRP (20 minute reaction time) as described above. The thickness of the polymer brush was 9.6 nm in DMSO, which was determined by AFM.

6. IMAGING AND ACTIVATION OF ACTIVE AND CONTROL SAMPLES

6.1 AFM Imaging

All mechanophore and control samples were characterized using an atomic force microscope (MFP-3D, Asylum Research Corp., Santa Barbara, CA). Silicon probes, AC 240-TS (Olympus America, Central Valley, PA) were used for imaging and activation. The nominal force constant of the probes was 1.7 N/m, with a resonant frequency of 70 kHz in air. Silicon probes were used in their original state, with a brief cleaning in ethanol and nitrogen drying before each experiment. All experiments were carried out in DMSO in a liquid cell. Before imaging, all cantilevers were calibrated on a clean Si (111) wafers.

In the DMSO media, the mechanophore features were imaged in contact mode with a load of 10-66 nN, with speeds ranging from 2.50-135.22 μm/s. The AFM images were acquired and

analyzed using Asylum MFP-3D software developed on the Igor Pro 6.34 platform.

6.2 Preparation of Silicon Wafers for Calibration

Polished silicon wafers were used to calibrate the cantilever before AFM imaging and activation. The wafers were cleaned by immersion in piranha solution for 30 minutes, and cleaned twice more with fresh piranha solution before being rinsed with copious amounts of milli-Q water. Cleaned wafers were subsequently stored in ultra-pure water, and rinsed with ethanol and dried under nitrogen before further use.

6.3 AFM Activation

Activation of the surface bound mechanophore was achieved using an atomic force microscope (MFP-3D, Asylum Research Corp., Santa Barbara, CA). The mechanophore samples were imaged under low forces [10-66 nN] until suitable areas were found. Silicon probes, AC 240-TS (Olympus America, Central Valley, PA) were used for activation by scanning with a high force (ranging from 200 nN to 1.0 μN) in contact mode in DMSO. After the high force scan, the areas were imaged again with low force scans to determine the extent of mechanophore activation.

6.4 AFM Custom Design Microlithography

Mechanophore regions were imaged at low contact forces (10-66 nN) using AFM to determine suitable areas for microlithography. Utilizing custom design software in Igor Pro 6.34, a bitmap image (either user designed or taken from the internet) was uploaded into the program, converted into greyscale and translated into force vectors. The color scale was assigned minimum and maximum force values, ranging from nanonewtons to micronewtons. Additional parameters, such as feature size, scan speed, lines per scan and scan angle were also specified. Feature

fabrication using this method typically took anywhere from 2-8 minutes, depending on feature size, scan speed and image line density. After the lithography scan was completed, the area was imaged again under low force with the same AFM tip to assess success.

7. FLUORESCENCE MEASUREMENT

Fluorescence images were acquired using a Cascade 512b high sensitivity camera, which was attached to Zeiss Axiovert 200M. A mercury lamp source was used with 360 nm centered/FWHM 11 nm band pass excitation filter, 410 nm pass dichroic mirror, and 420 nm/FWHM 20 nm band pass filter (Edmund Optics). For Figure 3 fluorescence measurements, the exposure time was set to 100 ms and 40x magnification on objective lens. Fluorescence images were processed with Image J.[7] Fluorescence intensity was measured by averaging over 20 μm x 20 μm region. Normalized photoluminescence (Figure 3 Right) was calculated by setting the average fluorescence intensity of 600 nN applied specimen to 100 and non-activated bare specimen as 0. For Figure 5 fluorescence measurements, the exposure time was 200 ms and 63x magnification on objective lens.

8. ToF-SIMS IMAGING

Active specimens that were subjected to a contact force of 450 nN were analyzed with ToF-SIMS (Physical Electronics PHI Trift III) imaging. For ToF-SIMS imaging, Au liquid source run with Au+ ion under static mode accelerated at 22 KeV energy was used as the source. Data was collected for 10 minute duration.

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