Supporting Information for:

Polymer Pen Lithography

Fengwei Huo,[1,2] Zijian Zheng,[1,2] Gengfeng Zheng,[1,2] Louise R. Giam,[2,3]

Hua Zhang,[1,2,§] and Chad A. Mirkin[1,2,3,*]

Fabrication of masters of polymer pen arrays:

Shipley1805 (MicroChem, Inc.) photoresist was spin-coated onto gold thin film substrates (10 nm Cr adhesion layer with 100 nm of Au thermally evaporated on a pre-cleaned oxidized Si <100> wafer). Square well arrays were fabricated by photolithography using a chrome mask. The photoresist patterns were developed in an MF319 developing solution (MicroChem, Inc.), and then exposed to O_2 plasma for 30 s (200 mTorr) to remove the residual organic layer. Subsequently, the substrates were placed in gold (Type TFA, Transene) and chromium (Type 1020, Transene) etching solutions, respectively. Copious rinsing with MiliQ water was required after each etching step to clean the surface. The photoresist was then washed away with acetone to expose the gold pattern. The gold patterned substrate was placed in a KOH etching solution (30% KOH in H_2O:isopropanol (4:1 v/v)) at 75 ˚C for ~25 min with vigorous stirring. The uncovered areas of the Si wafer were etched anisotropically, resulting in the formation of recessed pyramids. The remaining Au and Cr layers were removed by wet chemical etching. Finally, the pyramid master was modified with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (Gelest, Inc.) by gas phase silanization.

Fabrication of polymer pen arrays:

Hard PDMS (*h*-PDMS) *(S1, S2)* was used for fabricating the polymer pen arrays. The *h*-PDMS was composed of 3.4 g of vinyl-compound-rich prepolymer (VDT-731, Gelest) and 1.0 g of hydrosilane-rich crosslinker (HMS-301). Preparation of polymers typically required the addition of 20 ppm w/w platinum catalyst to the vinyl fraction (platinumdivinyltetramethyldisiloxane complex in xylene, SIP 6831.1 Gelest) and 0.1% w/w modulator to the mixture (2,4,6,8-tetramethyltetravinylcyclotetrasiloxane, Fluka). The mixture was stirred, degassed, and poured on top of the polymer pen array master. A pre-cleaned glass slide (VWR, Inc.) was then placed on top of the elastomer array and the whole assembly was cured at 70 ^{o}C overnight. The polymer pen array was carefully separated from the pyramid master and then used for polymer pen lithography experiments.

Patterning of protein arrays by polymer pen lithography:

Tetramethylrhodamine 5-(and-6)-isothiocyanate (TRITC) conjugated anti-mouse IgG arrays were generated on a Codelink™ glass slide (GE Healthcare) by PPL. In a typical experiment, we first modified the polymer pen array with polyethylene glycol silane (PEG-silane) to minimize non-specific interactions between the protein and PDMS surface. To effect surface modification, the polymer pen array was briefly exposed to an oxygen plasma (30 sec) to render the surface hydrophilic. Subsequently, it was immersed in a 1 mM aqueous solution of PEG-silane (pH 2, MW 2,000, Rapp Polymere, Germany) for 2 hr, cleaned with deionized water, and then blown dry with N_2. An aqueous solution consisting of 50 mg/ml glycerol and 5 mg/ml TRITC conjugated IgG was then spincoated onto the PEG-silane modified polymer pen array (1,000 rpm for 2 min), and the pen array was used to generate protein arrays on Codelink™ slides. The patterning environment was maintained at 20 ^{o}C and 70% relative humidity. After the PPL process, the Codelink™

slide was incubated in a humidity chamber overnight, and rinsed with 0.02% sodium dodecyl sulfate to remove physisorbed material. Fig. S5 shows the fluorescent image of the as generated 3×3 IgG arrays. Each IgG dot was made by contacting the tip array with the substrate for 3 seconds. The size of each IgG dot is 4 ± 0.7 μm.

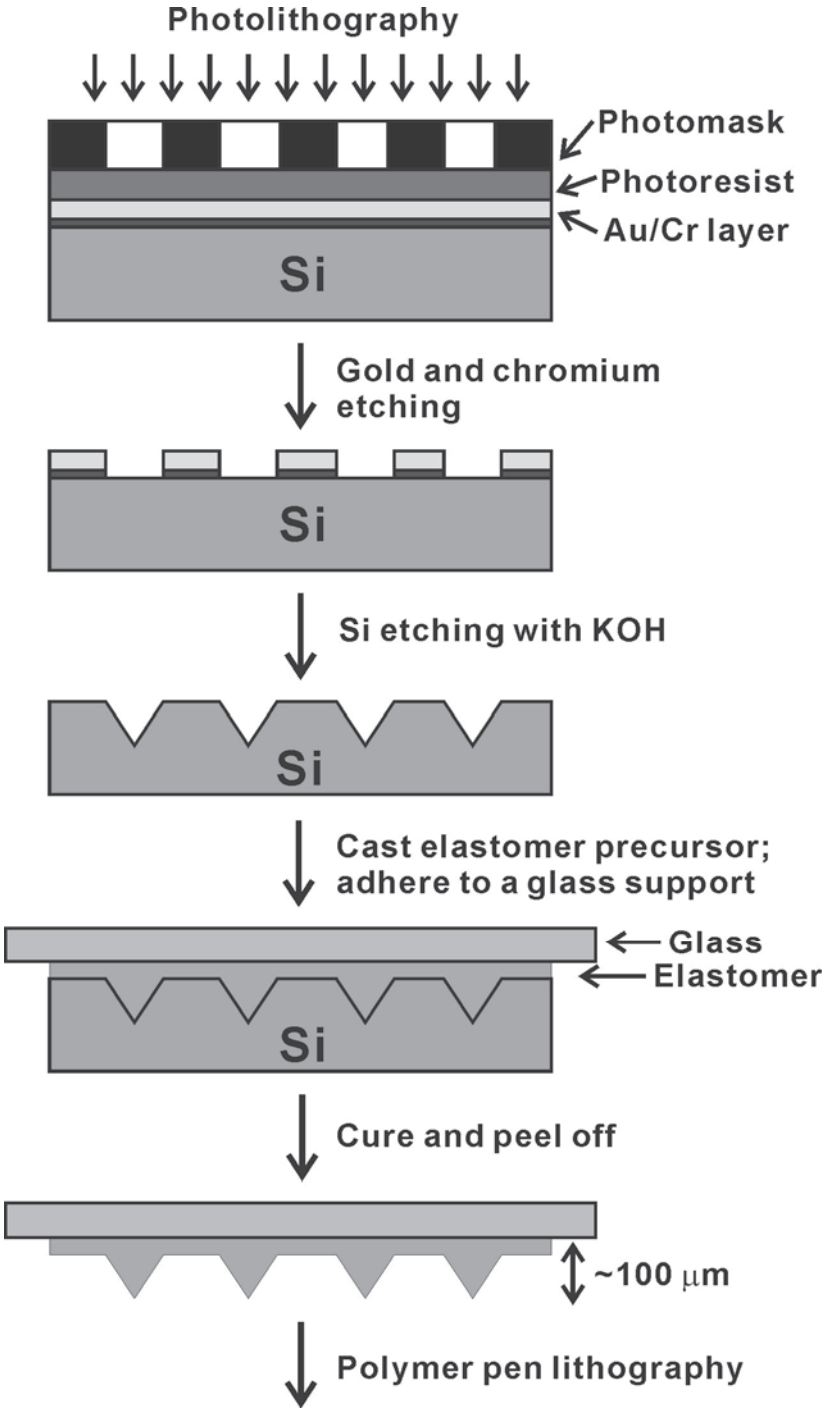

Fig. S1. Schematic diagram of the polymer pen array fabrication process.

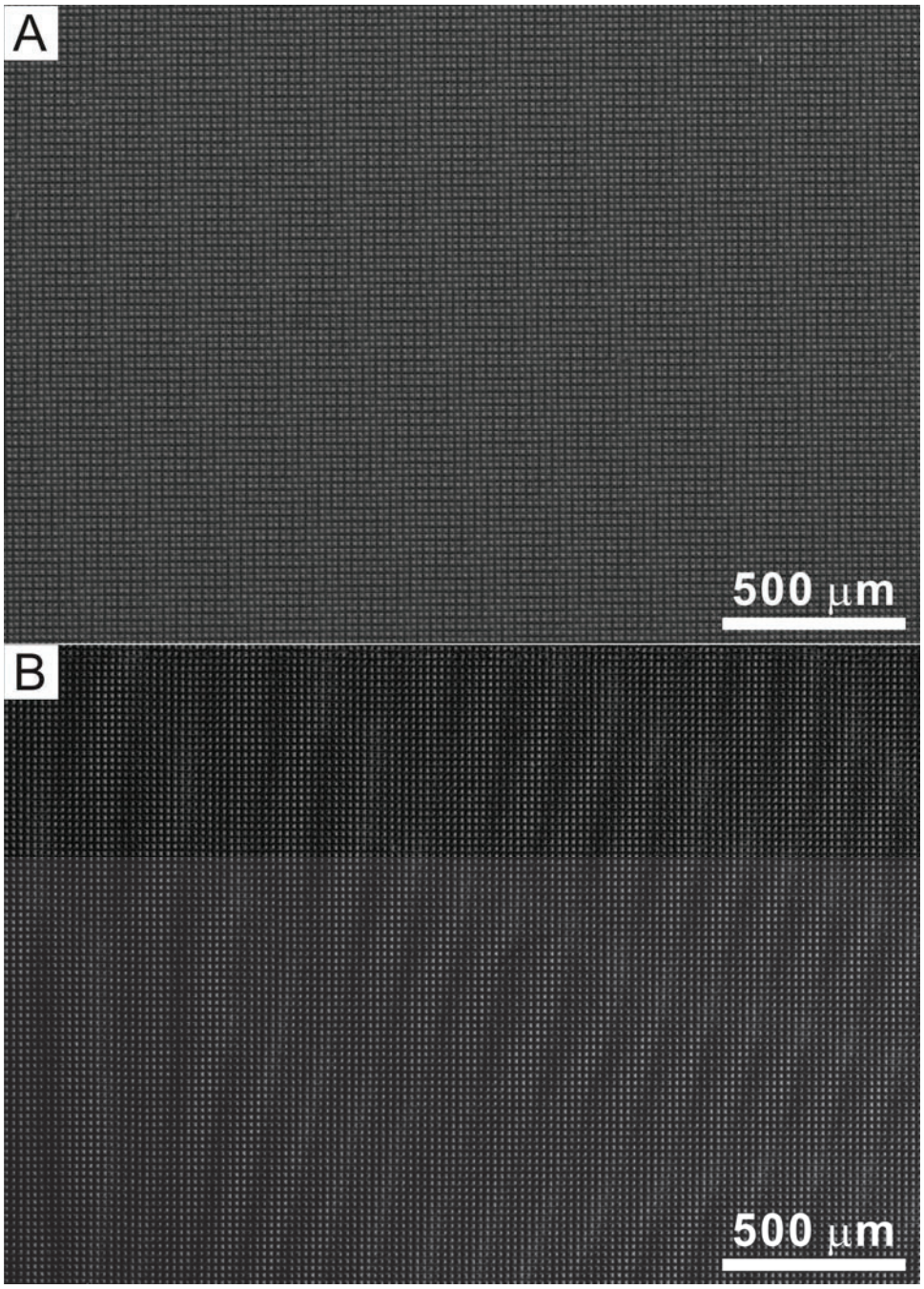

Fig. S2. SEM images of a polymer pen array **(A)** with and **(B)** without a glass support. The polymer pen array with a glass support is uniform across the whole area, while the one without a glass support is wavy.

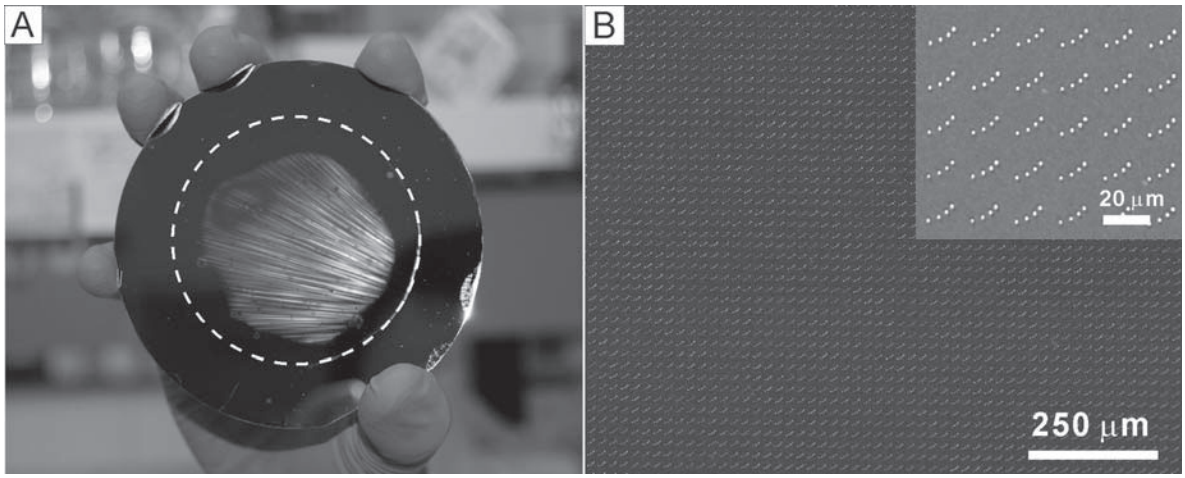

Fig. S3. (A) A photograph of an etched gold pattern on a 4 inch Si wafer fabricated by PPL using the 11-million pen array shown in Fig. 1B. The area patterned by the pen array is highlighted with a white dashed line. In the center of the pen array, greater than 99% of the pens uniformly deliver the MHA ink to the substrate during the PPL process and form well-defined structures. Reduced activity occurs on the periphery of the array, due to poor contact between the pens in the peripheral area of the array and the Si substrate. This arises from current instrument sample holder limitations. **(B)** Optical microscope image of gold patterns in **(A)** made by PPL. The inset is a zoom-in image. The image shows that every intended structure forms in this experiment.

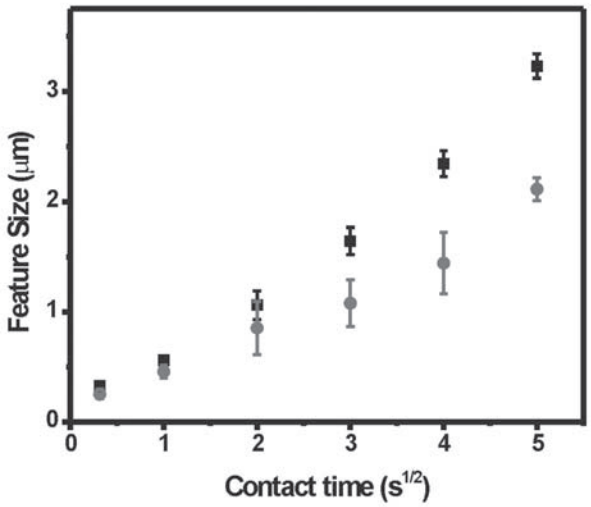

Fig. S4. MHA dot size as a function of tip-substrate contact time. Dot size increases with increasing tip-substrate contact time at constant contact force (initial contact). The results were obtained using a polymer pen array with 15,000 pyramid-shaped tips at a temperature of 23 ^{o}C and relative humidity of 50% (circles) and 90% (squares).

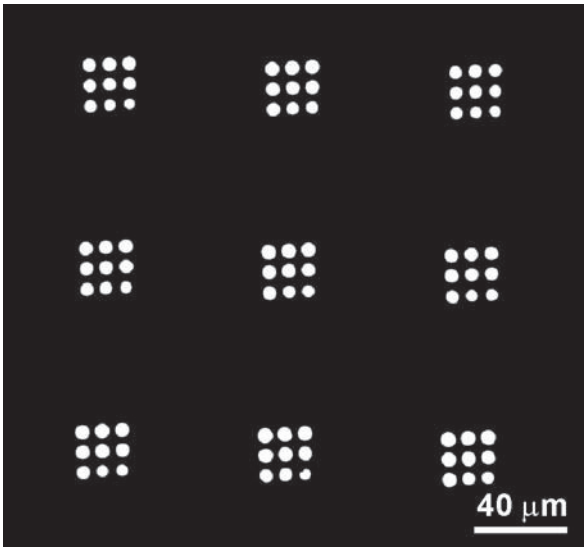

Fig. S5. Fluorescence microscopy image of Anti-Mouse IgG arrays fabricated by PPL.

References

S1. H. Schmid, B. Michel, *Macromolecules* **33**, 3042 (2000).

S2. T. W. Odom, J. C. Love, D. B. Wolfe, K. E. Paul, G. M. Whitesides, *Langmuir* **18**, 5314 (2002).