Supporting Information for

Polyethylene Glycol as a Novel Resist and Sacrificial Material for Generating Positive and Negative Nanostructures

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The comparative study of performance of polyethylene glycol (PEG) and 1-octadecanethiol (ODT) as resist for Au etching.

Experimental Section: To evaluate the PEG resist's performance in comparison with ODT, we studied pure monolayers of ODT and PEG arrays made by conventional microcontact printing and passivated with 1-octadecanethiol (ODT), pre- and post etching of the gold. Au- (35 nm) and Ti- (5 nm) coated n-type [100] silicon substrates were used for all experiments. SAMs of ODT were made by soaking a gold substrate in 1 mM ODT hexane solution for 20 min. Dot-shaped PEG structures (5 μm, diameter) were made with a PDMS stamp on a Au-coated silicon substrate. The exposed gold was subsequently passivated by soaking the substrate in a 1 mM ODT hexane solution for 20 min. (Figure S1)

Each substrate was immersed in an Au etching solution (20 mM thiourea and 30 mM iron nitrate nonahydrate aquatic solution, 70 °C) for 15 min. At this point, the pits formed from incomplete passivation of the gold are difficult to visualize by optical microscopy. They can be amplified by treating them with a silicon etching solution (KOH (26 g)/H_2O (113 mL)/*i*-PrOH (37 mL), 70 °C) for 30 min. Therefore, once the entire remaining gold coating is removed with aqua regia (2 min soaking), the number of pits on silicon substrate was counted. (Figure S3)

Reference

[1] X.-M. Zhao, J. L. Wilbur, G. M. Whitesides *Langmuir* **1996,** *12,* 3257-3264.

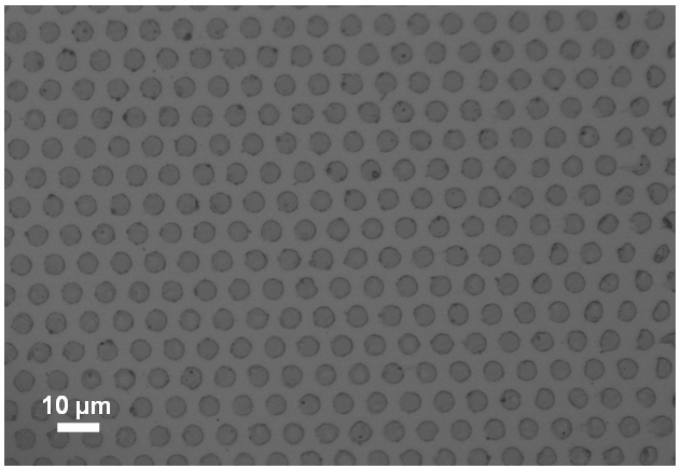

Figure S1. Optical microscope image of a PEG pattern (dots, diameter is 5 µm) on a Au-coated silicon substrate. PEG, dispersed in acetonitrile (5 mg/ml), was used for microcontact printing. The circular features are the PEG-coated areas.

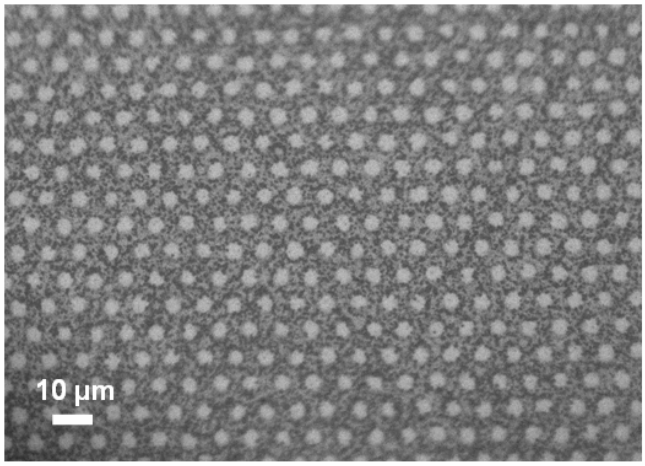

Figure S2 Optical microscope image of an ODT-passivated PEG pattern after attempting to etch the Au for 7 min. The PEG patterned areas are light contrast (raised) while the ODT areas are dark. The regions covered by PEG are more uniform in contrast than those covered by ODT. The ODT regions seem to show significant pitting.

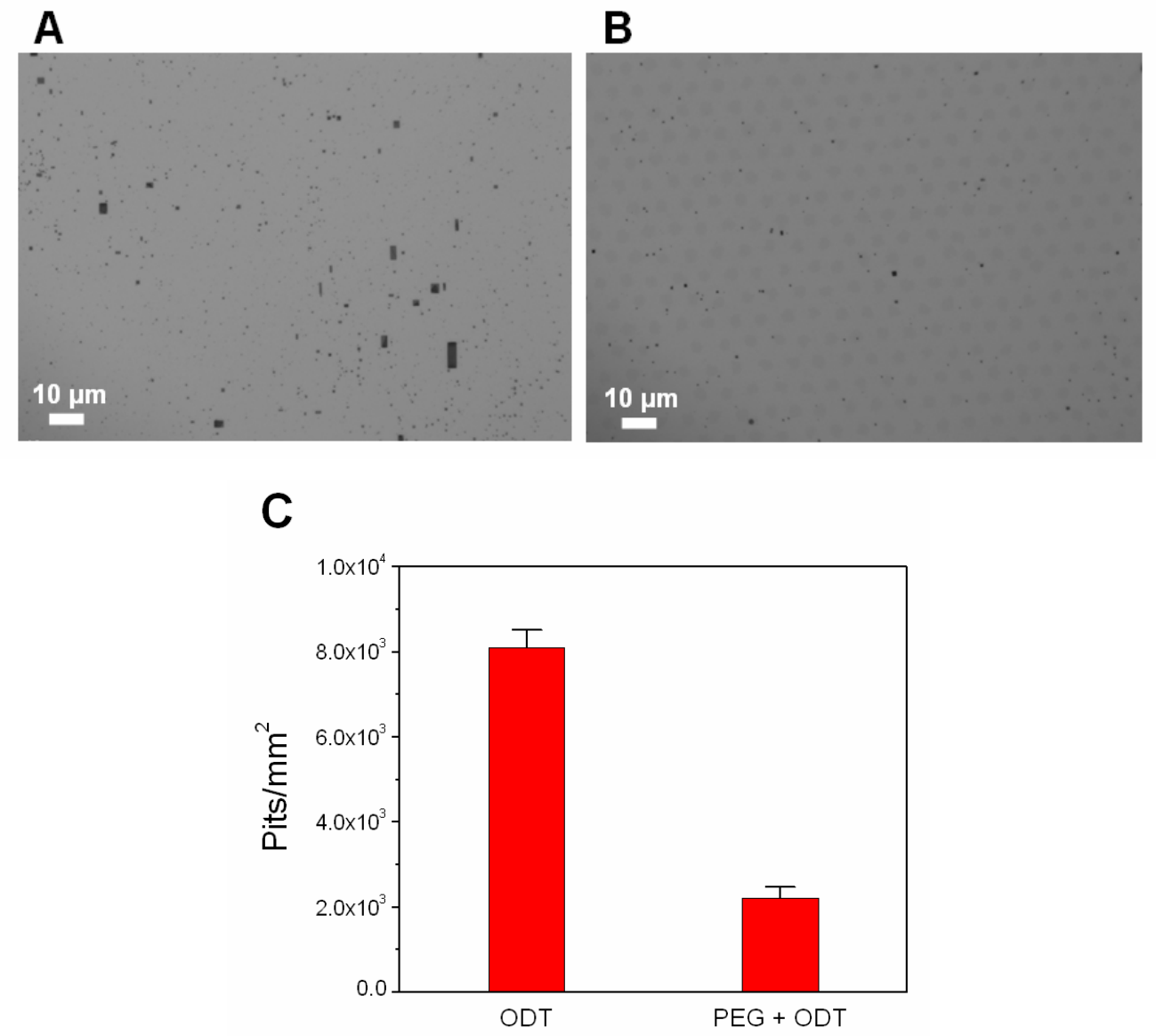

Figure S3 Optical microscope image of (A) an ODT SAM and (B) a ODT-passivated PEG pattern made by microcontact printing. Both images were obtained after Au etching for 15 min, silicon etching for 30 min, and metal etching by aqua regia for 2 min. (C) The density of pits/area (denoted by the dark spots) measured for an ODT SAM-coated substrate and an ODT passivated PEG pattern protected Au film. The ODT passivated PEG patterned substrate has significantly fewer pits than the ODT SAM-coated substrate. This experiment was repeated three times with similar results.

The relationship between feature height and dwell time.

To test the relationship between dwell time and PEG feature height, a dot array was generated by DPN under the conditions described in the main text of the manuscript except that a single AFM tip (Type A from NanoInk Inc., Skokie, IL) instead of a cantilever array was used. Dwell times of 16, 8, and 4 s were studied.

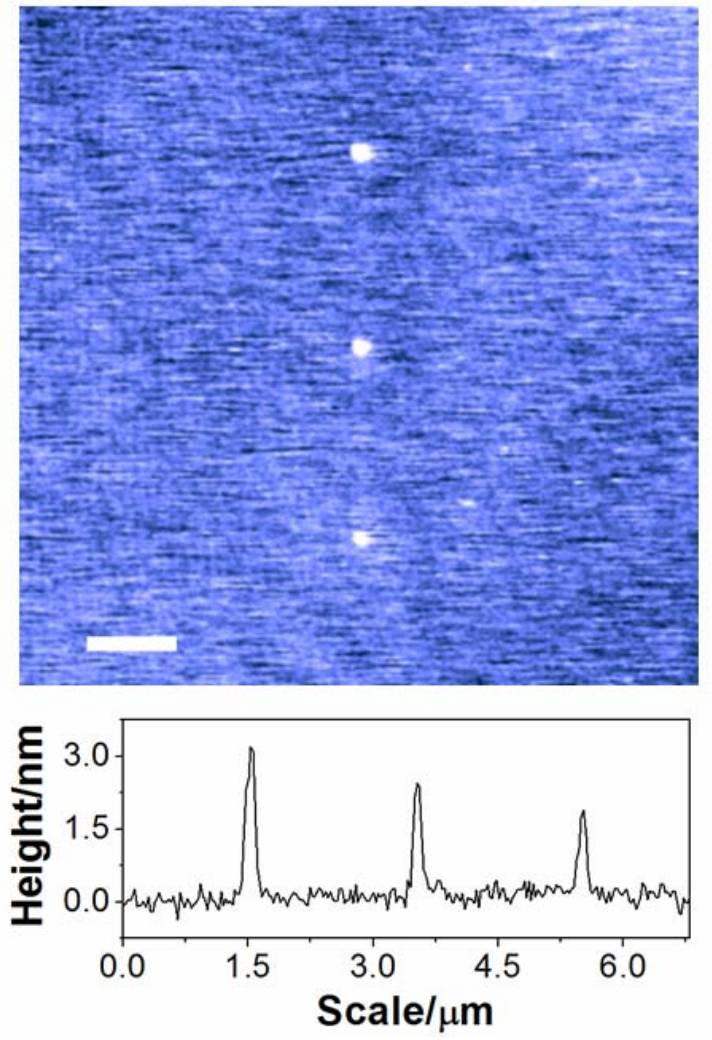

Figure S4 A typical contact-mode AFM topographic image and height profile of three dots generated with 16, 8, and 4 s tip-substrate contact times (top-to-bottom), respectively. Scale bar is 1 μm.