

Supporting Information

Formation and Surface Modification of Nanopatterned Thiol-ene Substrates using Step and Flash Imprint Lithography

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Experimental Details

Materials

All monomers were purchased from Sigma Aldrich (Milwaukee, WI) and used as received unless otherwise mentioned. The silanes n-octadecyltriethoxysilane (OTES) and 3-mercaptopropyltrimethoxysilane (MPTMS) were purchased from Gelest, Inc. (Morrisville). The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was purchased from Ciba-Geigy (Hawthorn, NY). All solvents were purchased from Fisher Scientific and used without any purification. The glass substrates used to form nanopatterns were precleaned, plain microslides obtained from Gold Seal Products (Portsmouth, NH). The fused silica wafer used for the fabrication of the mold was purchased from General Optics GSI Group.

Preparation of the mold

The mold was prepared using electron beam lithography and successive reactive ion etching. A super-polished fused silica wafer (diameter 12.7 mm, thickness 5.1 mm, rms roughness 0.1 nm) was cleaned with acetone and methanol and then coated with poly (methyl methacrylate) (PMMA) at a speed of 3000 rpm for a period of 40 seconds to deposit a PMMA layer of approximately 80 nm. The coated silica wafer was baked on a hot plate for 5 minutes at 180°C and then coated with a 10 nm aluminum layer by thermal evaporation to avoid charging during the e-beam writing process. A pattern approximately 80 μm X 100 μm with various features such as lines, squares and checkerboards of sub-micron dimensions was written on the PMMA layer using a scanning electron microscope (JEOL 6400) controlled by Nano Pattern Generation System (JC Nabity). After the e-beam writing, the aluminum film was removed using a dilute sodium hydroxide solution (5 drops of sodium hydroxide in 50 ml of water). The PMMA film was developed in a solution (methyl isobutyl ketone (MIBK) and isopropanol (IPA) (1:3 by volume)) for about 50 sec and then rinsed in another solution (MIBK and IPA (1:9 by volume)) for 20 sec. The wafer was then baked for 3 minutes at a temperature of 100°C. The PMMA pattern was etched into the silica substrate using reactive ion etching using octafluorocyclobutane (C₄F₈) plasma in an inductively coupled plasma etching system (MESC Multiplex ICP) with a chamber pressure of ~6.5 mTorr for 100 seconds. In addition, a square of approximately 2mm X 2 mm area was coated with chromium, centered around the patterned area. The rest of the mold substrate was etched a further 860 nm and the chromium-coated region was washed with the chromium

etchant. The lifted square is fabricated as an aid to faster identification of the patterned area on the mold and the replica for imaging purposes.

Deposition of Self-Assembled Monolayers (SAMs)

The patterned mold was coated with n-octadecyltriethoxysilane (OTES) SAM to reduce the surface energy and facilitate the removal of the nanopatterned replica following polymerization. The mold was cleaned in a Piranha solution (1:3 vol:vol mixture of hydrogen peroxide and sulfuric acid) for 45 minutes and washed with DI water and acetone and dried with nitrogen. The substrate was then immersed in OTES solution (~1 mM in toluene) at ~20°C for 30 minutes. The OTES solution was prepared in nitrogen gas environment to avoid degradation by water in the air. The substrate was then rinsed in turn with toluene, acetone, chloroform, and isopropanol. Finally, the SAM was annealed on a hot metal block kept at 150°C in vacuum (3×10^{-2} kPa) overnight.

MPTMS-coated glass slides were prepared using vapor-based SAM deposition method. Piranha-cleaned glass substrates were placed in a Teflon jar with a small amount (~0.5 ml) of OTES in a vial and the jar was purged with argon for 5 minutes. The Teflon jar was placed in an oven maintained at 90°C for 3 hours. The substrates were then removed from the jar, washed with toluene and acetone and dried with nitrogen.

Preparation of nanopatterned replicas

SFIL was used for the replication of the nano-patterned mold. A microscope slide was coated with MPTMS using the same procedure as described in the previous section. A thiol-ene resin consisting of a mixture of triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione

(triazine) and pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol), where the ratio of thiol to ene groups was 1.1:1, was prepared with 0.1% DMPA as photoinitiator. A drop of the monomer was sandwiched between a piece of the MPTMS coated glass slide and the mold and clipped at the edges using binder clips. The assembly was gently heated with a heating gun to make the monomer less viscous and exposed to UV light (365 nm, 15 mW/cm²) for 1 minute. The clips were then removed and the mold was held tightly in a custom-made holder. The glass substrate was gently separated from the mold, exposing the nanopatterned surface of the mold. The mold was then unclamped from the holder without damaging the smooth, patterned surface, and was subsequently washed with acetone and dried. The polymer with the imprinted nanopattern was attached to the glass piece due to the reaction with the surface thiol and covalently attached to the glass piece. The replica was washed with methanol and dried with nitrogen.

Modification of nanopatterned replicas

The nanopatterned replicas formed were modified with both linear and loosely cross-linked thiol-ene polymers. Thiol-ene monomers react in a stoichiometric fashion and the excess thiol added during the polymerization process results in the existence of unreacted thiols on the surface. A photopolymerizable monomer containing hexyl acrylate (HA) and 0.1 wt% DMPA was sandwiched between the replica and a glass substrate. A thin spacer (~50 μm) was placed between the replica and the glass piece. The assembly was exposed to UV light (365 nm, 15 mW/cm²) for 5 minutes and separated. The replica was washed with methanol after polymerization and dried with nitrogen. The same procedure was repeated with a monomer mixture containing HA and 10 mol%

octane thiol as well as with a mixture of triethylene glycol divinyl ether (DVE3) and tetrathiol where the ene to thiol ratio was maintained at 1:0.35. In the cases when thiol was present in the bulk, the polymerization time was 3 minutes. In the case of crosslinking monomers, the glass slide used for covering the monomer mixture was coated with a Teflon Amorphous Polymer (Dupont Fluoroproducts) solution to minimize adhesion of formed polymer and facilitate removal after polymerization.

A photomask with 50 μ m square pattern was used to photolithographically modify the substrates. The DVE3-tetrathiol mixture (ene:thiol = 1:0.35) with 0.01% DMPA was sandwiched between the mask and the replica and the nanopatterned polymer was exposed to collimated UV light (365nm, 15 mW/cm²) through on the photomask for 3 minutes.

Characterization of Nanopatterned Substrates:

All surfaces were imaged using contact mode Scanning Probe Microscopy using a PicoSPM II from Molecular Imaging Inc. (Phoenix, AZ). Tapping mode SPM was used to image the polymer substrates. A low vacuum scanning electron microscope (SEM, Jeol 6480LV) was used to obtain SEM images.

Additional images

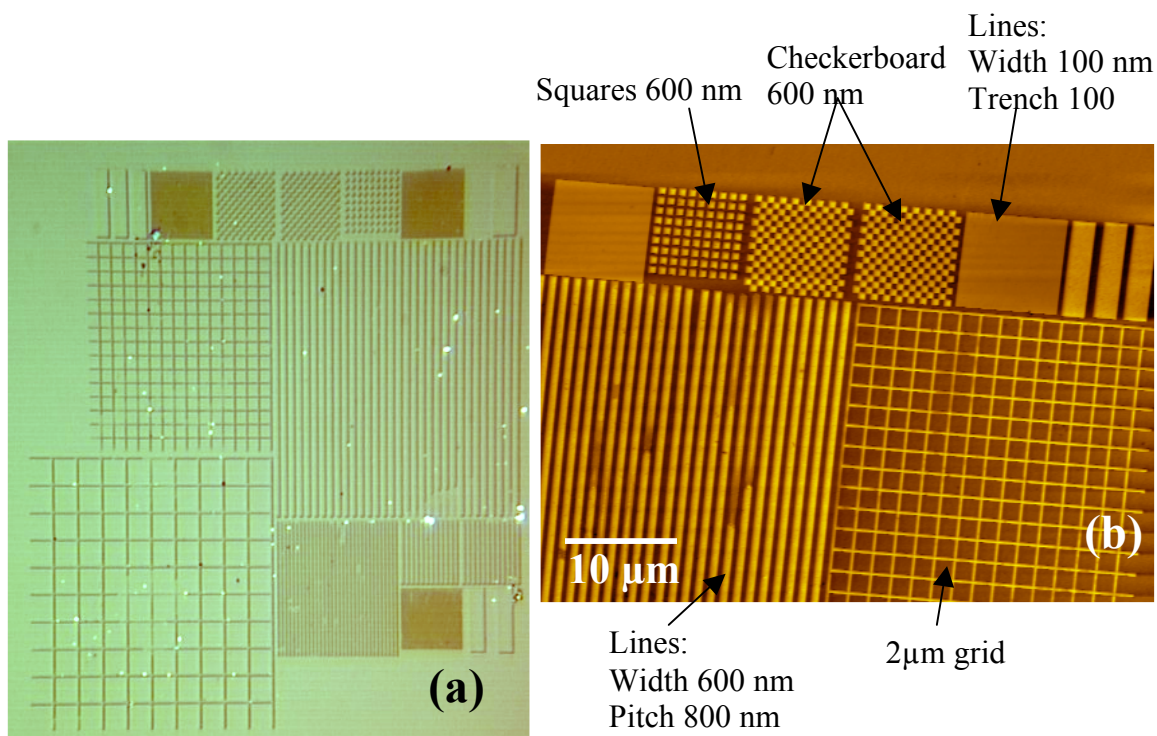


Figure S1. (a) Optical microscopy image of the mold used. (b) AFM image of the replica formed using SFIL. The monomer used was a mixture of tetrathiol and triazine where the thiol to ene ratio was 1.1:1 with 0.1% DMPA present as the photoinitiator. The monomer was polymerized by exposing to UV light (365 nm, 15 mW/cm²) for 1 minute.

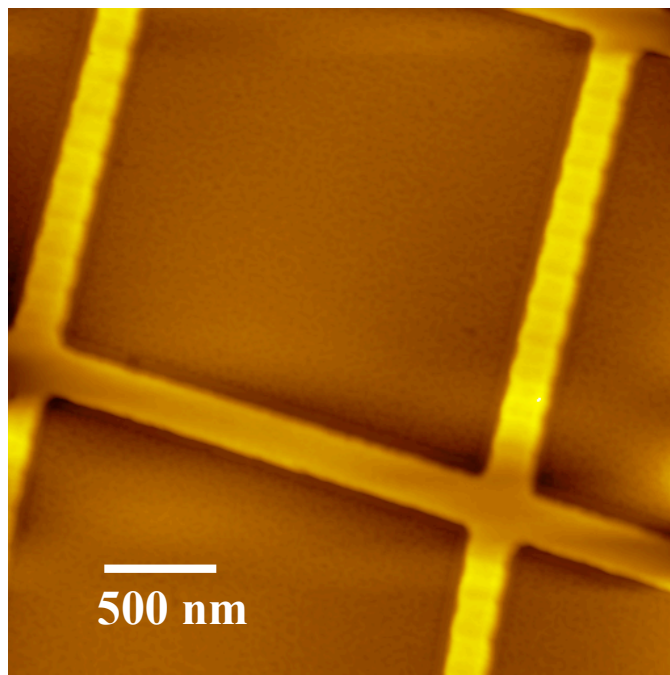


Figure S2. AFM image of an unmodified replica formed using SFIL with triazine-tetrathiol mixture (thiol:ene = 1.1:1) and 0.1% DMPA. The width of the patterned feature is 200 nm and was used to generate the profile of unmodified replica in Figure 3(b) in the manuscript.