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# Supplementary Information

# Ultralarge-Area Block Copolymer Lithography via Soft Graphoepitaxy

## *Photoresist Materials Requirements for Soft-Graphoepitaxy*

For successful soft-graphoepitaxy, the use of an organic negative tone photoresist is crucial. First, the negative tone photoresist layer crosslinked by UV photopatterning maintains its structural integrity as topographic confinement during the high temperature annealing required for the directed assembly of block copolymers. Second, owing to beam blocking by a photomask, the trench region of the photoresist pattern is not exposed to high energy UV radiation during photopatterning. Accordingly, the organic polymer brush or SAM layer deposited on the bottom surface of trench is not damaged and effectively directs the orientation (surface perpendicular or surface parallel) of anisotropic (cylinder or lamellar) self-assembled nanodomains. Third, the organic photoresist layer can be completely disposed of by a mild cleaning process, and this removal is a key feature for compatibility with conventional semiconductor fabrication processes requiring multi-layer overlay processing. In this work, SU8 was used as an organic negative tone photoresist. The photosensitive range of SU-8 is 300 to 400 nm, a region accessible with conventional I-line photolithography. Its high transparency in the near UV range allows the fabrication of high aspect ratio topographic patterns with vertical side wall profiles. SU8 has high heat/chemical resistance that minimizes the PR swelling by annealing process of the block copolymer and solvent of the block copolymer solution. Furthermore, A SU8 layer on a neutrally modified silicon substrate can be completely disposed by a mild cleaning process. Note that a polystyrene-*r*-poly(methyl methacylate) (PS-*r*-PMMA) copolymer brush layer plays a role as a release layer for stripping SU8 as well as a neutral layer.

## *Experimental Procedure of Soft-Graphoepitaxy*

***Substrate pretreatment:*** A silicon substrate was cleaned by immersion in piranha solution (7:3 mixture of $H_2SO_4$ and $H_2O_2$) for 1 hr at 110 °C and rinsing with deionized water. After cleaning, the surface tension of the substrate was neutrally modified by depositing a neutral polystyrene-*r*-poly(methyl methacylate) (PS-*r*-PMMA) copolymer brush layer. The brush layer covalently bonded to the silicon substrate was deposited through spin-casting and thermally annealed subsequently at 160 °C for 24 hr in a vacuum.

***Photoresist confinement preparation:*** A negative tone photoresist of SU8 (MicroChem Corp. US) was used to prepare topographic photoresist confinements. A photoresist layer was spin-coated on a neutrally modified silicon substrate and soft baked at 65 °C for 20 sec to evaporate residual solvent and densify the film. The photoresist film was exposed to an I-line source (Midas/MDA-6000 DUV, KR; wavelength: 365 nm; 9.5 $mW/cm^2$) through a pattern mask and post baked at 110 °C for 60 sec to selectively crosslink the exposed portion of the film. The pattern development was performed by immersing the exposed photoresist film into a propylene glycol methyl ether acetate (PGMEA) solution for 60 sec.

***Soft graphoepitaxy of PS-b-PMMA thin films by photoresist confinement:*** After photoresist patterning, a thin film of diblock copolymer was spin-coated over the topographic pattern. Diblock copolymers having molecular weights ($M_n$) of 48K kg $mol^{-1}$/46K kg $mol^{-1}$ or 52K kg $mol^{-1}$/52K kg $mol^{-1}$ for PS/PMMA blocks, respectively, were spin-cast from a toluene solution over the patterned substrate. Thermal annealing was conducted at 250 °C to accomplish directed assembly. After directed assembly, the PMMA component was selectively removed from the assembled block copolymer film by dry-etching with $O_2$ plasma. The resultant nanostructured polystyrene template within the photoresist pattern trench was used as a deposition mask for further pattern transfer.

***Fabrication of one-dimensional Au nanowire stack array:*** PMMA component in the soft-graphoepitaxially assembled block copolymer thin film was selectively removed by UV exposure and subsequent acetic acid washing. The aluminum (Al) nanowire array was produced by thermally evaporation of a 15 nm thick Al layer over a soft-graphoepitaxially assembled lamellar template. After deposition, the PS mask and photoresist pattern were completely removed by sonication in toluene.

***Chemical pattern preparation:*** Highly aligned graphoepitaxial morphology was used as a selective etching mask for the underlying neutral polymer bush layer. Since the etching resistivity of PMMA is significantly lower than that of PS or SU8 for oxygen plasma treatment, a mild oxygen etching over the entire area selectively etched the neutral brushes underneath the PMMA lamellae. This created a chemical nanopattern consisting of polar (bare substrate or oxygenated brush) stripes and neutral (unetched brush) stripes underneath the block copolymer film. Meanwhile, the brush layer under the photoresist layer remains unpatterned and neutral. Therefore, the finally obtained substrate pattern constitutes a hierarchical nanopattern of the alternate chemically nanopatterned region (400 nm width) and uniform neutral region (200 nm width). After this pattern transfer, the residual polymer and photoresist remaining on the substrate surface was thoroughly washed by a mild sonication in toluene.

***Ultralarge-area block copolymer lithography:*** Given that the chemically patterned substrate has been successfully prepared, ultralarge-area block copolymer lamellar alignment was simply achieved by spin-casting the same lamellar PS-*b*-PMMA block copolymer thin film (40 nm thickness; molecular weights ($M_n$) of 48K kg mol$^{-1}$/46K kg mol$^{-1}$ or 52K kg mol$^{-1}$/52K kg mol$^{-1}$ for PS/PMMA blocks) and epitaxial self-assembly upon thermal annealing.

***Characterization:*** The nanoscale morphology of block copolymer thin film and the fabricated metal nanowires were imaged using a Hitachi S-4800 SEM with a field emission source at 1 kV.