

# Directed Self Assembly of a Stable Radical Polymer

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*Primary CNF Tools Used: ASML DUV stepper, Oxford 80+ etcher, Oxford ICP Cobra etcher*

## Abstract:

We use graphoepitaxy and solvent vapor annealing (SVA) for directed self-assembly of a stable radical block copolymer composed of blocks of poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) and poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA). We report lamellar and cylindrical morphologies formed by SVA. Silicon substrate is topographically modified to form trenches with two different trench depths. Narrow and deep trenches are shown to assemble the blocks parallel to the trench direction, however with defects. By using a neutral underlayer, we show alignment of the blocks perpendicular to the trench direction. This ordering is further improved by increasing film thickness. Lastly, we study morphologies by using gold sidewalls instead of the silicon sidewalls for chemically heterogeneous graphoepitaxy. We thus demonstrate control over placement of stable radical groups in nanostructures controlled for further electrical characterizations and device fabrication.

## Summary of Research:

**Introduction.** Microphase separation of the block copolymers (BCP) result in the formation of chemically discrete domains ordered in various geometries [1]. Recently, stable radical BCPs have been studied in order to place these stable radical groups in such geometries and study charge transport in these polymers [2,3]. Commonly explored BCP morphologies include the cylindrical (hcp), lamellar, and spherical (bcc) microphases, which can be ordered in the scale of microns. Lamellar morphology BCPs are often utilized in BCP lithography, but their self-assembly typically results in a finger-print like pattern rather than unidirectional order [4]. Directed self-assembly (DSA) has been studied extensively to attain this unidirectional order in lamellar and down-lying cylindrical BCPs. Two common DSA techniques used are graphoepitaxy, which uses topographically patterned substrates and chemoepitaxy, which uses chemically modified substrates [5]. We use graphoepitaxy here to unidirectionally order the two blocks parallel and perpendicular to the trenches using the strategies shown in Figure 1.

**Methods.** The trenches and gold sidewall are formed by deep UV (DUV) lithography process. Antireflective coating (ARC) DUV42P was first spin-coated followed by the resist UV210. DUV exposures were performed using

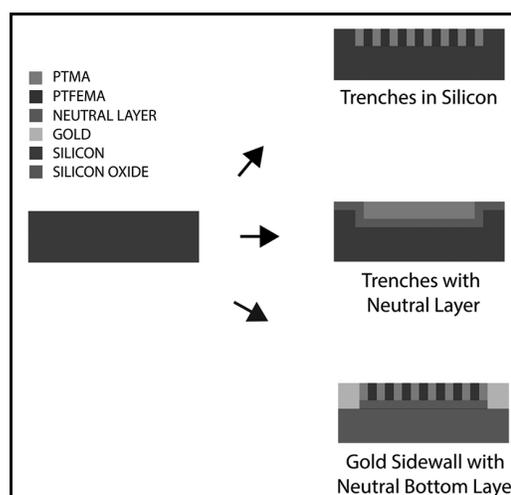


Figure 1: Epitaxial strategies used for direct self-assembly.

ASML 300C stepper. The dose was adjusted to achieve the desired trench width at a depth of focus of  $-0.1 \mu\text{m}$ . The exposed films were then baked at  $130^\circ\text{C}$  for 90s and developed using AZ MIF 726.

The ARC was then etched using Oxford 80+ etcher by using  $\text{CF}_4$  and  $\text{O}_2$  plasma. The silicon was then etched in Oxford Cobra ICP etcher using an HBr chemistry. The resist was then stripped using Anatech resist strip. Gold sidewalls were prepared using a lift-off process. A 300 nm thick  $\text{SiO}_2$  layer was grown on the silicon wafer by PECVD. The line and space patterns were created using the lithography process as mentioned above. ARC layer was then etched as mentioned above. A 5 nm layer of titanium and 100 nm film of gold were deposited on the patterned photoresist using an electron beam evaporator. The metal deposited on the photoresist was lifted off using MICROPOSIT 1165 solution. The BCP had a PTMA block molecular weight of 21,700 g/mol and PTFEMA block molecular weight of 14,300 g/mol having a dispersity of 1.21 when measured by GPC. AFM images were taken using Asylum-MFP3D-Bio-AFM-SPM in tapping mode.

### Results and Discussion:

The block copolymer when annealed using chloroform vapor for three hours exhibited a lamellar morphology as shown in Figure 2. The lamella showed short-range order in a fingerprint-like pattern and thus to enable DSA, we used trenches in the silicon wafer with a trench depth of 120 nm as well as gold sidewalls (100 nm thick). The AFM images are summarized in Figure 3. All films except the one shown in Figure 3e were annealed for six hours. The blocks align parallel to the silicon trenches but with defects as shown in Figure 3a and 3b. The defects exist due to weakly preferential wetting of silicon by PTMA. By grafting a neutral underlayer, we align the blocks perpendicular to the trenches (as shown in Figure 3c and 3d) with an improvement in the alignment with a thicker film. A short-range ordered parallel alignment is also obtained using gold sidewalls due to low vapor pressure annealing for three hours (Figure 3e).

Thus, we demonstrate directed self-assembly of the stable radical containing block copolymer in morphologies parallel and perpendicular to the trench direction. This opens up the possibility to elucidate charge transport in stable radical polymers and relate polymer structure to the electrical properties.

### References:

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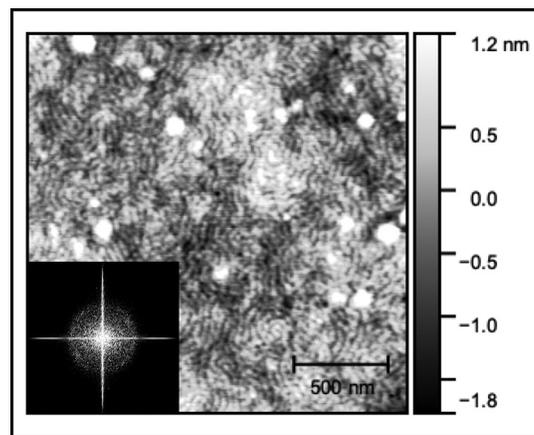


Figure 2: AFM topography image and its 2DFFT (inset) when annealed for three hours.

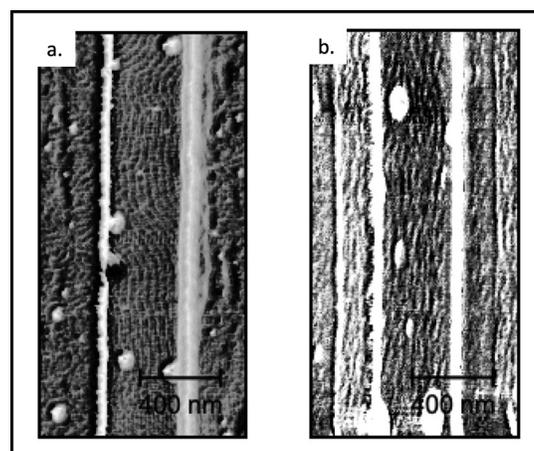


Figure 3: AFM phase images of the thin lm on (a) Si trench (width 480 nm) (b) Si trench (width 448 nm).

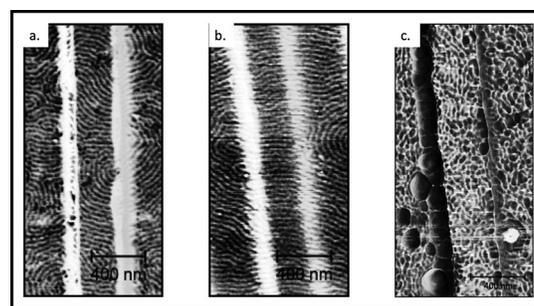


Figure 4: AFM phase images of the thin lm on (a) and (b) Si trench (width 480 nm) and (c) gold sidewall (width 448 nm).