Nanometer-Scale Area-Selective Formation of Polymer Brushes

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Primary CNF Tools Used: E-beam resist spinners, JEOL 9500, FilMetrics F50-EXR, Oxford 81 etcher, Zeiss Ultra SEM, optical microscope

Abstract:

The topological control of mixed polymer brushes can be realized via multi-steps surface-initiated polymerizations on a pattern fabricated by e-beam lithography, which is known for its fine resolution and precision. Patterned binary polymer brushes were produced on silicon wafers by area-selective deposition of two different initiators, using patterned e-beam resists as the masks. As a result, "nano-spikes" made of rod brushes were formed, surrounded by soft coil brushes. This platform has unique dual properties and thus can be used in various applications such as cytoskeleton mimicry and molecular recognition.

MATERIALS

Summary of Research:

Introduction. Polymer brushes are polymer chains that have one end covalently bonded to a substrate, such as a silicon wafer. Due to the unusual molecular arrangements, polymer brushes have demonstrated interesting surface properties and thus has been one of the main research focus in polymer science [1]. Potential applications such as metal oxide surface functionalization, optoelectronics, and medical diagnosis have been studied in the past decades. However, there is an increasing need for location-specific functionalization of these metal oxide surfaces as patterning techniques advances in the lithography industry. As such, incorporating e-beam lithography with the vapor phase surface-initiated polymerization can be a possible solution to the aforementioned demands.

Previously we have reported a new approach to nano-pattern rod-like polymer brushes with high persistence length using the equipment in Cornell NanoScale Facilities (CNF). This year we have made further advancement by incorporating our knowledge in combining rod-coil polymer brushes in a single system, which will provide enhanced phase separation and unique mechanochemical surface properties [2]. This report provides a novel pathway in fabricating nano-patterned rod-coil mixed polymer brushes on a silicon wafer, which will result in surfaces with dual properties, chemical functionality, and responsive behavior under different stimulations.

Fabrication. The mixed polymer brushes were patterned on a silicon wafer by multi-steps fabrication process and area-selective deposition of surface-bound initiators for polymerizations.

E-beam Resist Mask Preparation. Patterned e-beam resist mask (~150 nm) was prepared through JEOL 9500. The sample was then etched ~ 10 nm using Oxford 81 etcher to remove residual debris in the unmasked area.

Synthesis of the Rod Brushes. The deposition of a silane initiator on the treated substrate was carried out in a closed chamber under vacuum and elevator temperature. The initiator was allowed to vaporize and thus reacting with the exposed metal oxide surfaces. Afterward, the resist mask was removed by organic solvents. Subsequently, surface-initiated ring-opening polymerization of poly-*y*-benzyl-*L*-glutamate (PBLG), a rod-like polymer, was synthesized under vacuum and elevated temperature.

Synthesis of the Coil Brushes. The deposition of α-bromoisobutyryl bromide (BiBB) functionalized silane initiator was deposited onto the remaining unreacted area under similar conditions, followed by surface-initiated atom-transfer radical polymerization of poly(*N*-isopropylacrylamide) (PNIPAM), obtaining a thermo-responsive coil polymer brushes with low persistence length.

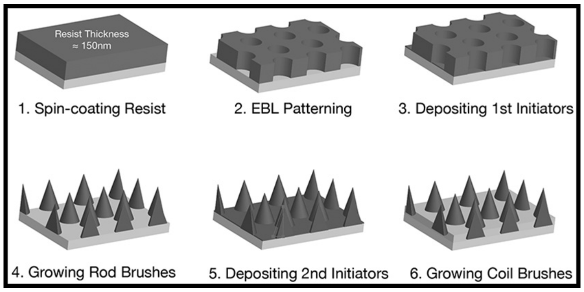

Figure 1: Schematic illustration of the fabrication process.

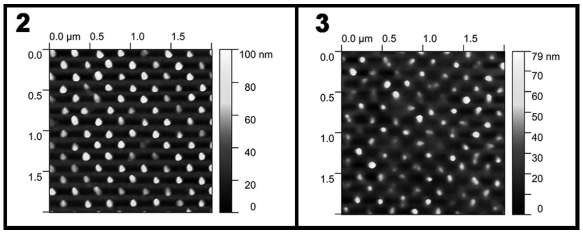

Figure 2 left: *AFM image of the patterned PBLG rod brushes.*
Figure 3, right: *AFM image of the mixed PBLG-PNIPAM brushes.*

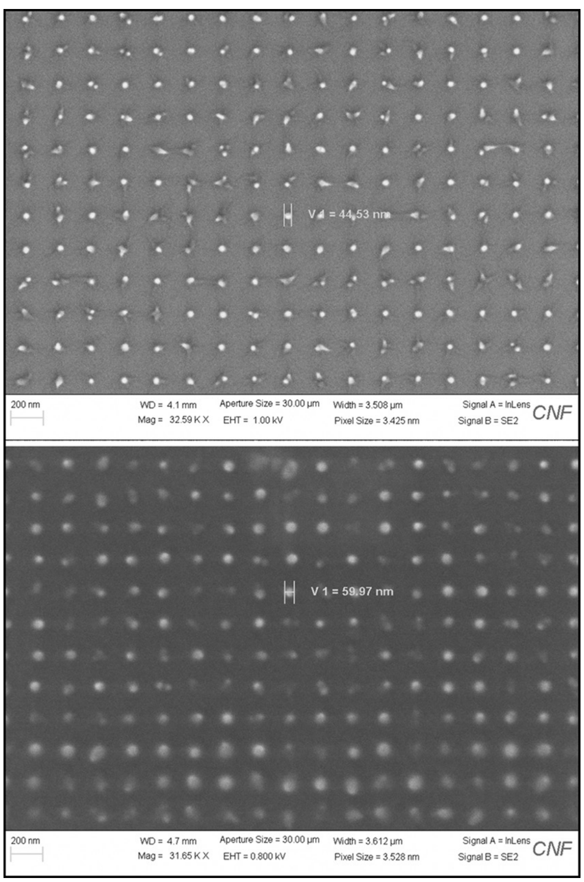

Figure 4: SEM images of the PBLG brushes (top) without PNIPAM and (bottom) with PNIPAM brushes.

A schematic illustration of the whole fabrication process is shown in Figure 1.

Characterization and Results:

The e-beam resist thickness was measured by FilMetrics F50-EXR. The patterned e-beam resist was examined using Zeiss Ultra SEM. The patterned PBLG rod brushes were characterized using atomic force microscopy (AFM) for height measurement (Figure 2), and Zeiss Ultra scanning electron microscopy (SEM) for topological analysis. The resulting surfaces with mixed rod-coil brushes were analyzed with AFM (Figure 3) and SEM (Figure 4) to compare the differences.

In conclusion, we demonstrated a process for precisely control the spatial arrangement of mixed rod-coil polymer brushes. In the near future, we plan to examine how the addition of thermo-responsive PNIPAM brushes in the system would affect the surface properties. We also plan to explore the use of these surfaces for biological applications, such as cell membrane support and molecular recognition.

References:

[1] Chen, W. L.; Cordero, R.; Tran, H.; Ober, C. K., 50th Anniversary Perspective: Polymer Brushes: Novel Surfaces for Future Materials. Macromolecules 2017, 50 (11), 4089-4113.

[2] Tran, H.; Zhang, Y.; Ober, C. K., Synthesis, Processing, and Characterization of Helical Polypeptide Rod-Coil Mixed Brushes. ACS Macro Lett 2018, 7 (10), 1186-1191.