Nano-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, Oxford 81

Abstract:

Polymer brushes can be formed in a location-specific manner via an integrated fabrication of surface-initiated polymerizations and electron-beam lithography, which is a state-of-art patterning tool known for its fine resolution and precision. Dot-patterned polymer brushes was produced on silicon wafers by area-selective deposition of initiators, using patterned e-beam resists as the masks. As a result, "nano-spikes" made of polypeptide (rod) brushes and "blurry bundles" of polystyrene (coil) brushes were formed via two different kinds of surface-initiated polymerizations. This platform can be useful for various applications such as cytoskeleton mimicry and molecular recognition.

Summary of Research:

Introduction. Polymer brushes are polymer chains that have one end covalently anchored to a flat substrate, such as a silicon wafer, with a high grafting density. Due to the unusual molecular arrangements and surface attachments, polymer brushes have exhibited unique surface properties and thus has an active research area in polymer science [1]. Potential applications such as organic thin film devices, optoelectronics, and medical diagnosis have been studied in the past decades. However, there is an increasing need for area-selective functionalization of metal oxide surfaces (for e.g. device fabrications) as lithographic techniques and nanofabrication advance. As such, making nanopatterned polymer brushes by incorporating e-beam lithography with the vapor phase surface-initiated polymerization can be one possible solution to these demands.

In addition to the polypeptide brushes, we have fabricated different polymer brushes by utilizing a new type of living polymerization into the integrated process, which will widen the potential of surface functionalities as well as fundamental studies of polymer brushes.

Fabrication. The polymer brushes were patterned on a silicon wafer via an integrated 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 ~ 40 nm using the 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 elevated temperature. The initiator was allowed to vaporize and thus react with the exposed metal oxide surfaces. Afterward, the resist mask was removed by organic solvents. Subsequently, surface-initiated ring-opening polymerization of poly-γ-benzyl-*L*-glutamate (PBLG), a rod-like polymer, was synthesized under vacuum and elevated temperature.

Synthesis of the Coil Brushes. After the deposition of silane initiator, there was one additional step of modifying these surface initiators with allyl 2-bromo-2.methylpropionate (BiBB), which acts as the activation site for the subsequent polymerization. Polystyrene (PS), a coil-like polymer, was then synthesized via surface-initiated Cu(0) mediated controlled radical polymerization (SI-CuCRP) under argon-protected environment and elevated temperature. Similar process was also carried out for other coil brushes such as poly(methyl methacrylate) (PMMA) to test the fabrication's adaptability.

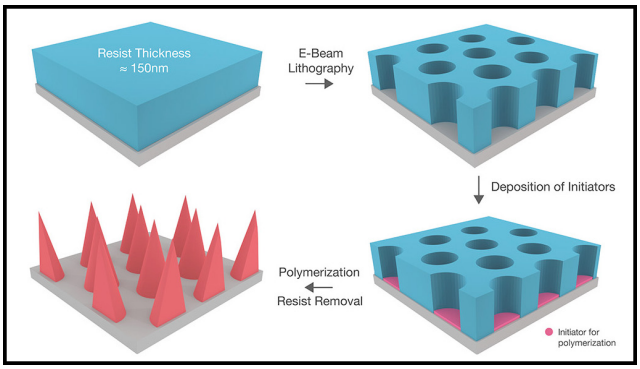

Figure 1: Schematic illustration of the fabrication process.

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 (Figure 2), the patterned PBLG brushes (Figure 3) and PS brushes (Figure 4) were characterized using Zeiss Ultra scanning electron microscopy (SEM) and Veeco Icon Atomic Force Microscope (AFM) for topological analysis.

Conclusion and Future Steps:

In conclusion, we demonstrated a novel process for precisely control the spatial arrangement of different kinds of polymer brushes. In the near future, we plan to examine how the surface topography varied with different kind of polymers in terms of molecular structures and physical properties. We also plan to explore the use of these surfaces for various applications, such as cell membrane support, biological simulated model and magnetic storage platforms.

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] Zhang, T.; Du, Y.; Müller, F.; Amin, I.; Jordan, R., Surface-initiated Cu(0) mediated controlled radical polymerization (SI-CuCRP) using a copper plate. Polym Chem-Uk 2015, 6 (14), 2726-2733.

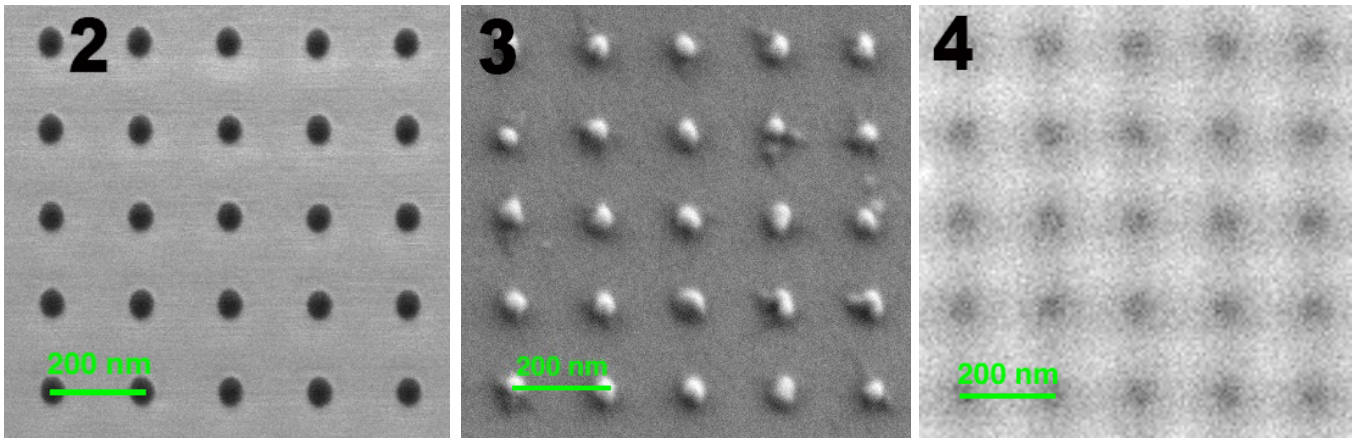

Figure 2, left: SEM of patterned e-beam resist. Figure 3, middle: SEM of the patterned PBLG rod brushes. Figure 4, right: SEM of the patterned PS brushes.