Introduction:
The control of the physicochemical properties of surfaces represents a fundamental issue in numerous applications ranging from coating technology and biotechnology to microelectronics [1-4]. Additionally, advances in biotechnology depend on the ability to fashion materials with precise control of feature size and functionality. Two common fabrication techniques include “top-down” and “bottom-up” approaches. The "top-down” approach utilizes photo or electron beam lithographic techniques [5]. The “bottom-up” approach utilizes self-assembling materials to produce surfaces ordered at the nanoscale level (~10 nm) [6].

Polymer brushes take advantage of this technique as they are well suited for the fabrication of nano or micropatterned arrays with controlled chemical functionality, shape, and feature dimension and inter feature spacing on the micron and nanometer length scale [7]. These characteristics make polymer brushes attractive for a variety of biotechnological applications including their use in molecular recognition, biosensing, protein separation and chromatography, combinatorial chemistry, scaffolds for tissue engineering, and micro- and nanofluids [7].

We use a combination of these “top-down” and “bottom-up” approaches by utilizing electron beam lithography (EBL) and surface-initiated polymerization (SIP). Classic electron beam resist, PMMA, is first spin coated onto a silica wafer and patterned using EBL. The pattern is transferred onto silicon by molecular vapour deposition of a silane monolayer followed by resist removal. Bare silicon regions are then “back-filled” with TEMPO functionalized self-assembled monolayers, and subsequently used for surface initiated polymer brush growth by nitroxide mediated controlled radical polymerization.

Summary:
We utilize “top-down” and “bottom-up” approaches to pattern polymer brushes at nanometer length scales. Electron beam resist, PMMA, was spin coated on a silica wafer and patterned using electron beam lithography. Following molecular vapour deposition of a silane monolayer, the resist was removed and bare silicon regions were “back-filled” with TEMPO functionalized self-assembled monolayers. Subsequent surface-initiated polymerization (SIP) brush growth via nitroxide mediated controlled radical polymerization produced a highly structured surface ordered at the nanoscale level (20 nm and 80 nm lines). These resulting surfaces with periodic chemistries may provide an exciting opportunity to bridge the gap between the limits of current lithographic methods (> 50 nm) and the need to achieve nanostructures as small as 10 nm. The ability to control chemical functionality and feature dimensions of these surfaces may lead to further advances in fields like nanobiotechnology and microelectronics.

References:
[1] Swalen, JD; Allara, DL; Andrade, JD; Chandross, EA; Garoff, S; Israelachvili, J; McCarthy, TJ; Murray, R; Pease, RF; Rabolt, JF; Wynne, K.; Yu, H. Langmuir 1987, 3, 932.
Surface Initiated Radical Polymerization on Patterned Surfaces: Convergence of Bottom-Up and Top-Down Lithography

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Figure 1, opposite:
Reaction scheme for the controlled growth of brushes on prepatterned surfaces. After E-beam lithography the pattern is transferred onto silicon by molecular vapour deposition of a silane monolayer followed by resist removal. Bare silicon regions were “back-filled” with TEMPO functionalized self-assembled monolayers and subsequently used for surface initiated polymer brush growth.

Figure 2, opposite left:
AFM image and cross section after vapor deposition of the silane monolayer.

Figure 3, opposite right:
AFM image and cross section after growth of Polystyrene brush.

Figure 1

Figure 2

Figure 3