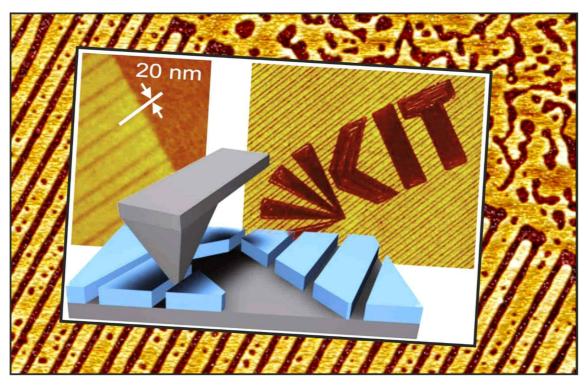
Tip-Induced Nanopatterned Polymer Brushes for Directed Self-Assembly of Polymer Blends and Transfer into Silicon Structures



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AFM patterned ultrathin surface films can serve as templates for nanoparticle positioning, targeted self-assembly of molecular structures, or arrangement of the lateral morphology of block copolymer films. In commonly used SAMs, either the tip is heavily worn or the molecules are not completely removed. Polymer brushes are chemically defined polymer chains grafted onto solid substrates using a simple physical process. We investigate mechanical AFM nanostructuring (m-SPL) of 2 nm thick vinyl-terminated polystyrene (PS) brushes on silicon substrates. Molecular heteropatterns generated with polymer blend lithography (PBL) allow evaluation of line broadening due to tip wear. We directly compare the patterning properties of the brush with those of a silanebased fluorinated SAM, and show that lines with widths of 20 nm (FWHM) can be stably written over lengths exceeding 20,000  $\mu$ m. We observe a factor of 5000 reduction in tip wear compared to experience on uncoated SiOx surfaces and hypothesize that the brush acts as a molecularly thin sliding layer, enabling a 5000-fold increase in tip lifetime. At the same time, brush molecules are bound weakly enough that they can be reliably removed with the highest accuracy. We present Polymer Phase Amplified Brush Editing (PPABE), which serves as a pattern template for RIE etching of the silicon substrate, with which structure depth enhancements of a factor of 50 compared to the original AFM structure in the brush layer could be achieved. [1]

We are currently working on a method where the ultra-thin resist layers are structured with t-SPL instead of m-SPL. We expect significantly longer write lengths, which means that the forces required for structuring and therefore the mechanical load on the tip could be significantly lower than with m-SPL. The challenge here is to achieve sufficient heat input to the monolayer for desorption, as the substrate (typically silicon) dissipates the heat very effectively and therefore layers close to the substrate cannot be heated up enough. This heat dissipation process is also the reason why a thin residual layer always remains in standard t-SPL, which then has to be removed by plasma treatment.

[1] R. Gröger, T. Heiler, Th. Schimmel, S. Walheim: Tip-Induced Nanopatterning of Ultrathin Polymer Brushes, Small, 2204962 (2023).