Electron beam lithography using grafted polystyrene monolayer brush

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Polymer brush is a thin mono-layer of polymer grafted onto a substrate, and is frequently utilized to modify the substrate surface properties including surface energy, adhesion, biocompatibility and friction[1]. Unlike spin-coating of a (thick) resist, polymer brush can be grafted (or physically adsorbed via, e.g., hydrogen bonding) onto irregular surfaces, and if the brush material is an e-beam resist, can be applied to pattern such irregular surfaces[4]. Previously we have shown electron beam lithography on irregular (non-planar) surfaces including optical fibers and AFM cantilevers using evaporated polystyrene resist[2,3] and grafted PMMA brush[4]. However, vacuum deposition system is costly, and most resists cannot be coated using thermal evaporation. As for PMMA brush resist, it has a positive tone that results in recessed structure after pattern transferring since exposed area will be removed after development. On the other hand, because it is only a mono-layer brush, lift-off cannot be performed using PMMA brush to fabricate protruded structures such as pillars. Therefore, a negative resist brush is required for patterning protruded structures on irregular surfaces.

Here we will show that a mono-layer polystyrene (PS) brush can be reliably grafted (or perhaps adsorbed via hydrogen bonding, rather than grafted via chemical bonding) on substrates like Si, SiO_2, Al and Cr, and can be employed to pattern these substrates by electron beam lithography. Using carboxyl (-COOH) terminated polystyrene, the brush is grafted onto a hydroxyl (-OH) terminated surface in a way similar to forming PMMA brush[4].

To form a mono-layer brush, oxygen plasma was applied to clean the substrate after solvent cleaning, and subsequently the substrate was spin-coated with PS-COOH dissolved in toluene at a concentration of 1%. Then the resist film was annealed at 160ºC for 24 hours to induce the grafting/adsorbing of the brush layer. Next, the bulk of the film was washed away in toluene which leaves behind a monolayer. The monolayer PS brush was successfully grafted on substrates mentioned above and the thickness of the monolayer was measured as approximately 15 nm.

Because the monolayer is too thin for pattern transfer, a sacrificial hard mask layer (here aluminum) was utilized. As shown in Figure 1, after PS brush grafting onto aluminum, electron beam exposure was carried out. Unlike chain-scission PMMA resist, solvent cannot be used to dissolve the unexposed yet grafted PS layer. Therefore, we developed the sample thermally[5] at 300ºC for 1 min that will preferentially degrade/desorb the unexposed thus linear PS brush. Next, diluted hydrofluoric acid was utilized to etch the aluminum, with less or negligible etching at the area protected by the exposed thus cross-linked PS brush. Finally, the pattern was further transferred into the silicon substrate using dry plasma etching with Al as mask. The SEM images of the completed structures are shown in Figure 2. The process can be applied to irregular substrates[4], with potential application in areas including (AFM) tip-enhanced Raman spectroscopy for chemical analysis[6] and lab-on-fiber technology[7].

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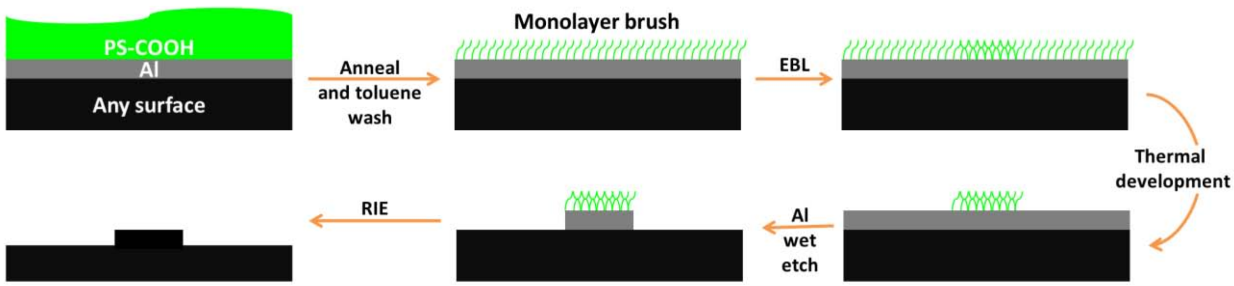

Figure 1. Process steps for patterning substrates using PS monolayer brush as negative resist.

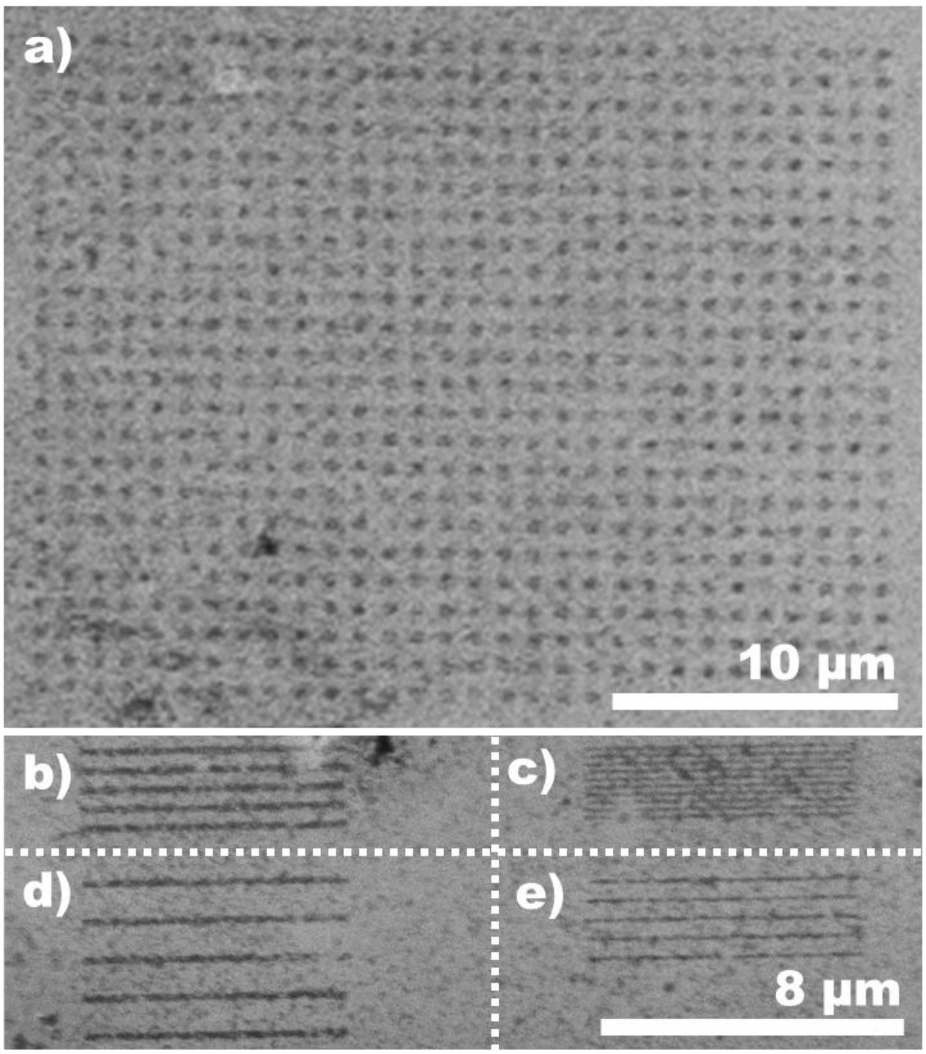

Figure 2. SEM images of the completed structure. (a) Pillar array with 1 µm period; (b-e) Line array with respectively 200 nm line-width 500 nm period, 100 nm line-width 200 nm period, 200 nm line-width 1 µm period, and 120 nm line-width 500 nm period. The structure was not very well defined presumably because the cross-linked PS monolayer brush could not fully protect the underneath Al against HF etching, and thus further process optimization is needed.