Enhanced adhesion of electron beam resist by grafted monolayer PMMA brush

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The performance of electron beam lithography is not only limited by "intrinsic" properties of the resist, notably the sensitivity and contrast, but also by "extrinsic" factors, such as the adhesion to substrate. Currently, the record densest line array pattern with array periodicity down to 9 nm was obtained by Berggren's group using HSQ resist, rather than using PMMA that has slightly higher contrast. This is because exposed HSQ becomes effectively silicon dioxide that is more rigid than organic polymer resist and it adheres strongly to the substrate, whereas ultra-narrow PMMA lines would be deformed and detached from substrate due to capillary force during liquid drying. Therefore, it is critical to modify the substrate surface in order to promote adhesion by the resist.

Here we modified the substrate surface by grafting a monolayer of PMMA brush that led to a remarkable improvement in resist performance. The brush is grafted onto a surface terminated with hydroxyl (–OH) group in the same way as forming the PMMA-r-Polystyrene brush that is widely used to provide a neutral surface for self assembly of diblock copolymer PMMA-b-Polystyrene. To form a mono-layer brush [1], the surface to be coated was coated with PMMA (contains 1.6% MAA, (meth)acrylic acid, to further promote the grafting process as MAA contains the desirable –COOH group). Next, the resist was annealed overnight at 160^{o}C to induce the chemical reaction between –OH on the resist and -OH on the surface, which led to the production of water and chemical bonding between the resist and substrate (–CO-O-Si- for silicon substrate). Finally, the bulk of PMMA was washed away by acetic acid, leaving behind a monolayer "brush".

To see the effect of this brush layer on lithography performance, we first studied ZEP resist using MIBK:MEK developer, for which we have achieved ultra-high sensitivity of 2.6 $\mu C/cm^2$, but not high resolution due to resist structure detachment when using this relatively strong developer [2]. As shown in Figure 1, the effect of the PMMA brush layer was very evident, and a well-defined dense line array of 100 nm period was achieved using this high sensitivity developer.

The second resist we studied is polystyrene [3-5] for which the adhesion to bare silicon wafer is much weaker than PMMA. As seen in Figure 2, the PMMA brush greatly improved the lithography performance, and a remarkably dense line array of 60 nm period was obtained.

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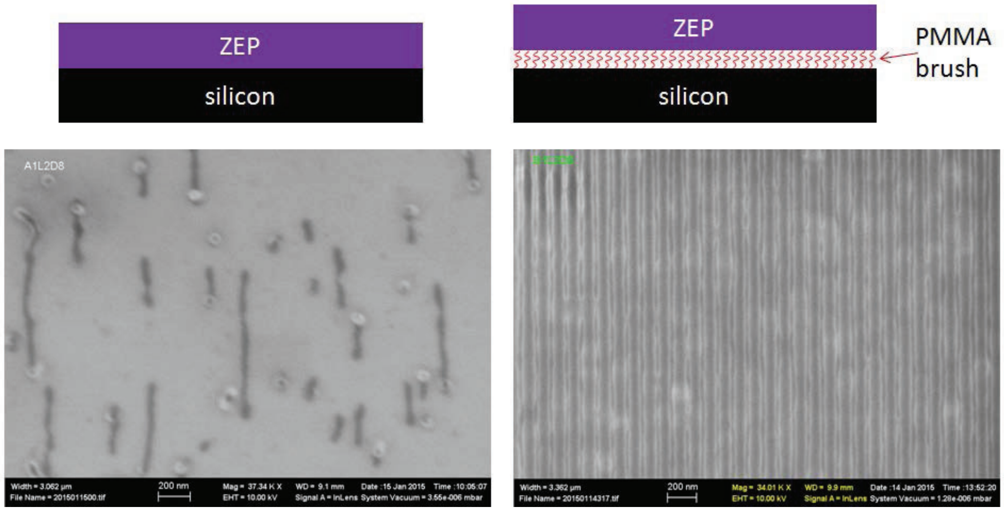

Figure 1. SEM images of 100 nm period line array exposed in ZEP resist with the same dose, coated on (left) bare silicon wafer and (right) silicon wafer grafted with PMMA brush. Resist lines were almost all detached from the bare silicon wafer (left image), because the MIBK:MEK developer, which offers much higher sensitivity, attacks the resist more aggressively than the usual high resolution developer (amyl acetate or xylene).

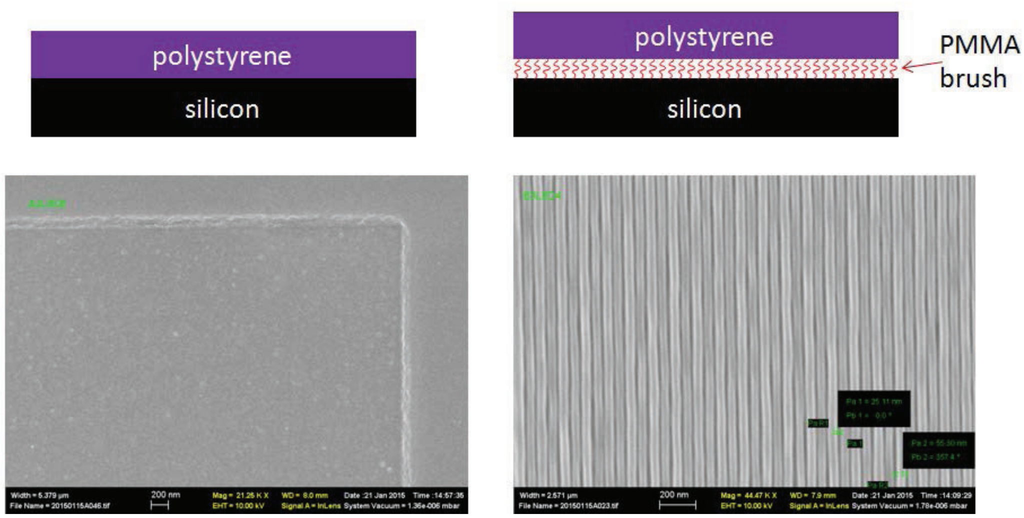

Figure 2. SEM images of 60 nm period line array exposed in 30 kg/mol polystyrene resist with the same dose, coated on (left) bare silicon wafer, and (right) silicon wafer grafted with PMMA brush. The resist lines were all detached from the bare silicon wafer (left image) due to capillary force during drying of the rinsing liquid. The resist was 80 nm thick and was developed using THF for 1 min.