Grafted PMMA mono-layer brush as negative tone e-beam resist

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Polymer brush is a mono-layer of polymer that is grafted onto a substrate. Previously, PMMA brush was shown to be used as a positive-tone electron-beam resist[1]. Unlike conventional resist coating methods such as spin coating, polymer brush having very uniform thickness can be applied on non-flat or irregular substrates, which can be used for many applications such as atomic-force microscope tips for tip enhanced Raman spectroscopy[2], or lab-on-fiber technology[3]. However, in order to fabricate protruding structures using polymer brush, a negative-tone resist is necessary because polymer brush is too thin to be used for lift-off process.

Though PMMA is well known to behave as negative resist when exposed at very high dose, the challenge for our process is that solvent can no longer be used as developer because it cannot dissolve the unexposed brush chemically bonded to the substrate. In this work, we overcame this issue by using dry thermal development[4].

The schematic drawing of the process steps is shown in Fig. 1. The PMMA brush is grafted onto a substrate in the same way as our previous work[1], using PMMA containing 1.6% methacrylic acid (MAA). Here the –COOH group in MAA reacts with the –OH group on the substrate with the release of water when annealed at 160 °C for 24 hours. After e-beam exposure at 3 keV and at 1000 - 2500 μC/cm^2, the brush layer was developed thermally at 340 °C for 1 minute instead of using solvent to achieve a negative tone. At this temperature, the unexposed or lightly exposed PMMA are degraded and desorbed, but the heavily exposed and thus cross-linked PMMA remains. For pattern transfer, since the mono-layer brush of ~10 nm thick is not sufficient as etching mask, we used an intermediate hard mask layer of 5 nm Al for pattern transfer into the substrate by wet chemical etching of Al using a mixture of H_3PO_4, CH_3COOH, HNO_3, and H_2O, and dry etching of the substrate (here silicon). As a proof of concept, Figure 2 shows the SEM images of line arrays etched into silicon fabricated by this process. The structures were not very well defined, so further process optimization is needed. Nanostructure fabrication on optical fiber and AFM probe is under way and will be presented.

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[3] Consales M. et al. *ACS Nano*, 6, 3163 (2012).

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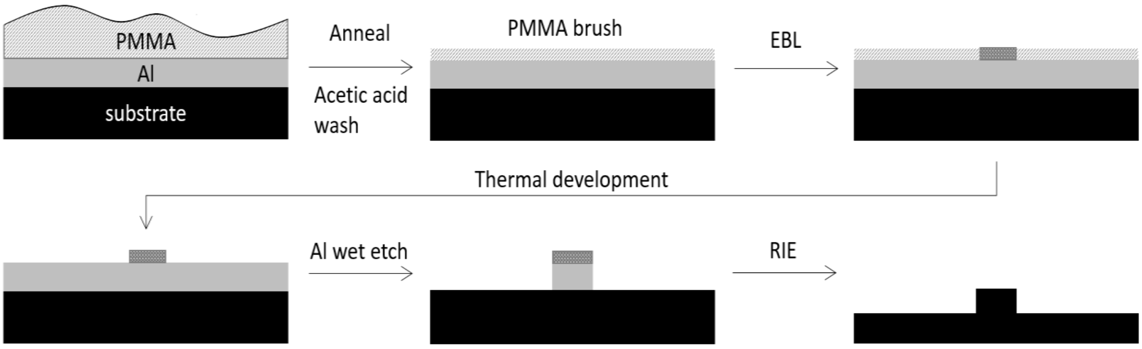

Figure 1. Process steps for patterning substrates using PMMA monolayer brush as negative resist. The PMMA can be coated by spin or dip coating, with non-uniform thickness for irregular surfaces. But after washing away the bulk film by acetic acid, the remaining monolayer brush has very uniform thickness.

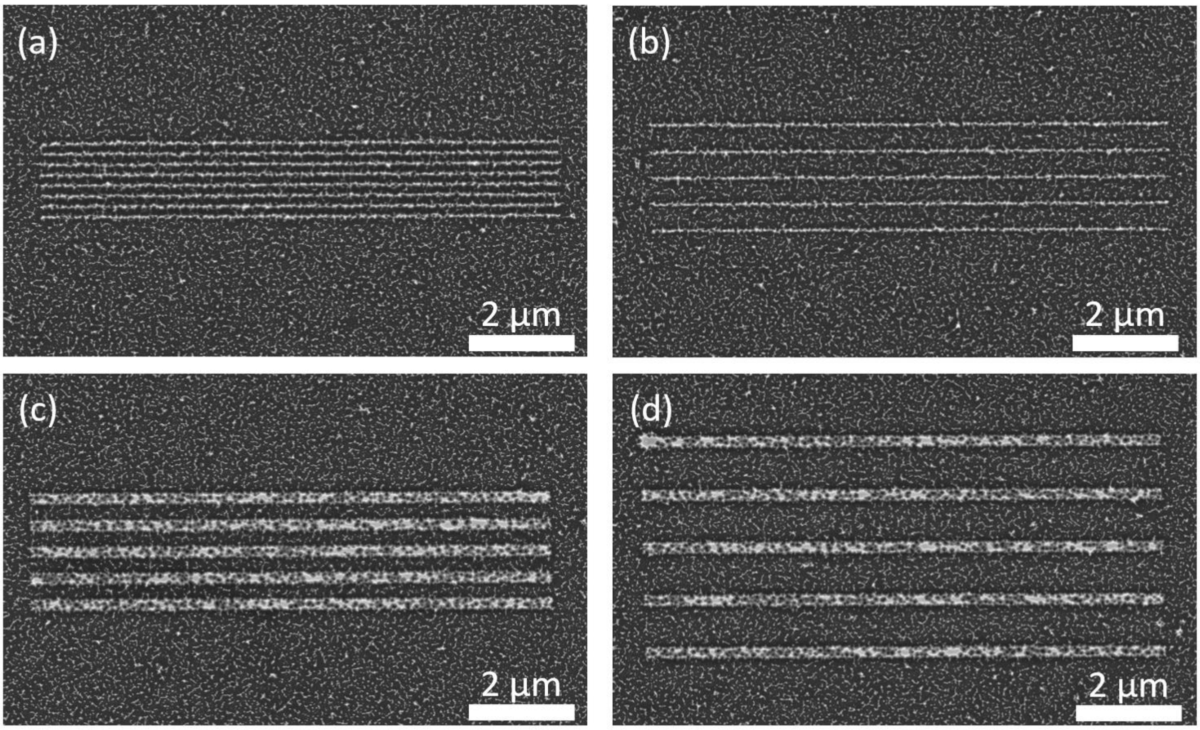

Figure 2. SEM images of line arrays on silicon substrate. (a) 100 nm line-width, 250 nm period, (b) 100 nm line-width, 500 nm period, (c) 250 nm line-width, 500 nm period, and (d) 250 nm line-width, 1 µm period.