Why So Negative?
Ways to make PMMA useful as a negative tone resist in electron beam lithography.

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Poly(methyl methacrylate) or PMMA, is the most commonly used e-beam lithography resist, but only as a positive-tone resist. It is well known that at high dose levels PMMA forms a cross-linked polymer, which performs as a negative-tone resist, but this is usually considered an unwanted side effect, best to be avoided. There are, however, properties of the cross-linked PMMA which can make it a useful fabrication step, as long as a few pitfalls are avoided. Some of these useful properties and the solutions to the pitfalls will be discussed.

In this work a Raith Voyager was used to expose PMMA 950K with 50KV accelerating voltage. The dose that is needed for forming the cross-linked PMMA was studied with different thicknesses, and it is shown that the film starts forming at $9mC/cm^2$ and it reaches maximum thickness at ~ $25mC/cm^2$. This thickness saturates at 60% of the starting spin-coated PMMA film thickness. Using such high doses (10-50 times of the doses needed to clear PMMA) can be very time consuming, unless high currents are used. Fortunately such currents are available in the Voyager and other modern EBL machines. Figure 1a shows an optical image of the results of exposing 5X5 micron squares onto 500nm PMMA with a 12nA beam applying doses between $15\text{-}30mC/cm^2$. The resist surface is deformed due to local beam damage. This damage can be avoided by exposing the squares with a different dose setup: fixing the dose to $1mC/cm^2$ and then exposing the squares multiple times until the required dose is reached. This increases the beam speed by an order of magnitude, resulting in a smooth uniform PMMA surface (Fig. 1b). Precise control of the dose can result in good control of the resulting thickness.

Using this method can be pushed toward smaller sizes, but when the squares become smaller and closer than ~200nm the pillars collapse and stick together (Fig 2a). This collapse can be avoided by using critical point drying to dry the sample instead of the usual nitrogen flow (Fig 2b).

Other notable properties of the negative resist are insolubility in acetone, higher melting temperature and slightly different reaction to etching which can lead to higher shape fidelity (Fig 3). Combining these properties with other resist and/or metal deposition can lead to interesting 3D structures, some of which will be shown (Fig. 4).

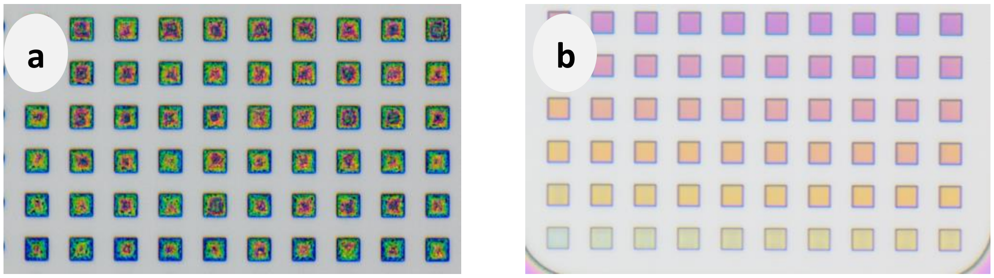

Figure 1: Effects of local damage of a 12nA beam exposing 15 to 24mC/cm^2 .
a) simple exposure b) exposure by repeated loops of *1mC/cm^2* . The square size is 5X5micron.

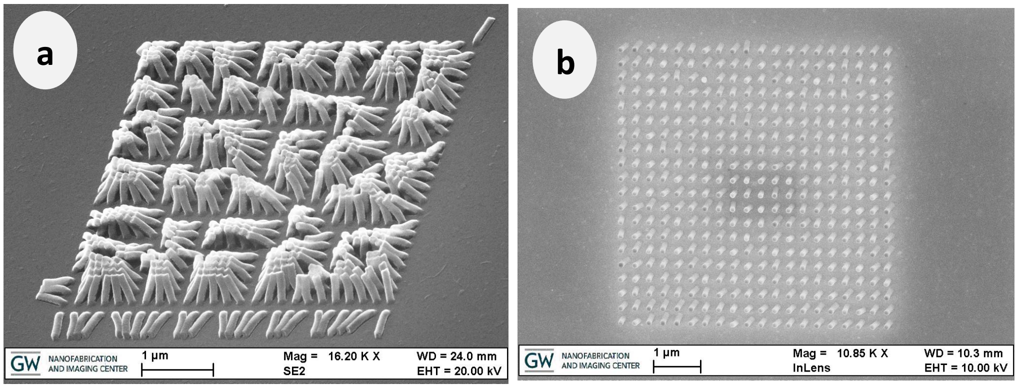

Figure 2: using Critical Point Drying to avoid resist pillar collapse. 100nm squares of negative resist with gaps of 200nm. a) nitrogen drying b) CPD drying.

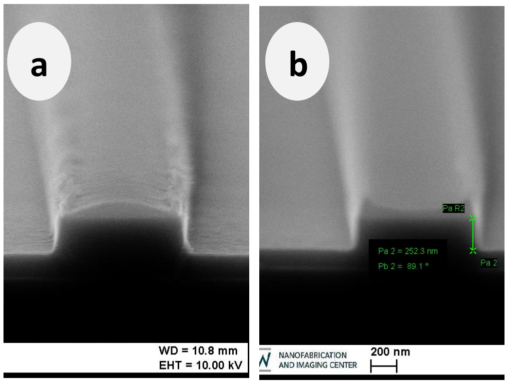

Figure 3: different shape during SiN etch.
530nm thick PMMA used as a mask for SiN etch. a) positive resist . b) negative.

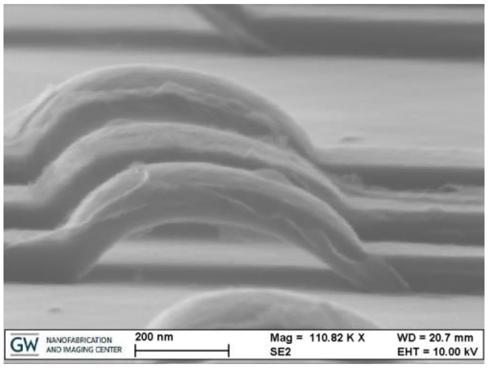

Figure 4: Titanium Bridges.
a structure formed by using both types of PMMA.