

# Improving PMMA Etch Resistance using Sequential Infiltration Synthesis

Y.C. Tseng, Q. Peng, L.E. Ocola, D. Czaplewski, J.W. Elam, S.B. Darling  
*Argonne National Laboratory, Lemont, IL 60439*  
*ytseng@anl.gov*

Pattern transfer using polymer-based resist materials has been difficult because of the low resistance of the polymers to plasma etching. In order to serve directly as an etch mask to fabricate high aspect-ratio structures, the resist film needs to be thick. However, high-resolution lithography requires thin resist films to minimize image blur. Usually, the pattern in the resist layer is first transferred to a hard mask layer that provides greater etch resistance. This complicates the fabrication process and leads to additional image blur, feature bias and line edge roughness. This has motivated recent work to improve the etch resistance of high resolution e-beam resists, such as PMMA and ZEP, by subsequent processing.<sup>1</sup>

In this work, we show that the etch resistance of poly(methyl methacrylate) (PMMA) can be improved by sequential infiltration synthesis (SIS). In this approach, the developed PMMA layer is reacted directly with trimethyl aluminum and water, the same precursors for depositing Al<sub>2</sub>O<sub>3</sub>, in an atomic layer deposition (ALD) chamber (figure 1). The resulting material shows substantial etch resistance to an HBr-based Si etch recipe, having an etch rate one-tenth of single-crystal silicon, without increase in line edge roughness or change in pattern dimensions found in silylated resists.<sup>3,4</sup> Figure 2 shows that the improvement in etch resistance enables the fabrication of trenches deeper than 150 nm in silicon, with a starting PMMA film only 33nm thick. In comparison, the unreacted PMMA alone provides little etch resistance.

Our previous work showed that the Al<sub>2</sub>O<sub>3</sub> does not simply deposit on top of the resist layer, but rather infiltrates the bulk of the layer.<sup>2</sup> Energy dispersive X-Ray (EDX) imaging of the mask material shows the presence of aluminum after 2 min of HBr/O<sub>2</sub> etching. The remaining mask is much thinner than the starting thickness, yet still has a large amount of aluminum. This indicates that the reaction between PMMA and the ALD precursors has occurred far below the surface of the PMMA layer. This approach for improving etch resistance of PMMA enables the fabrication of high-aspect ratio features in silicon, without the need for an intermediate hard mask. The low thermal budget of the SIS process also makes it compatible with most microelectronic fabrication processes. The wide variety of resist / SIS precursor combinations should make this process applicable to virtually limitless types of resist and substrate materials.

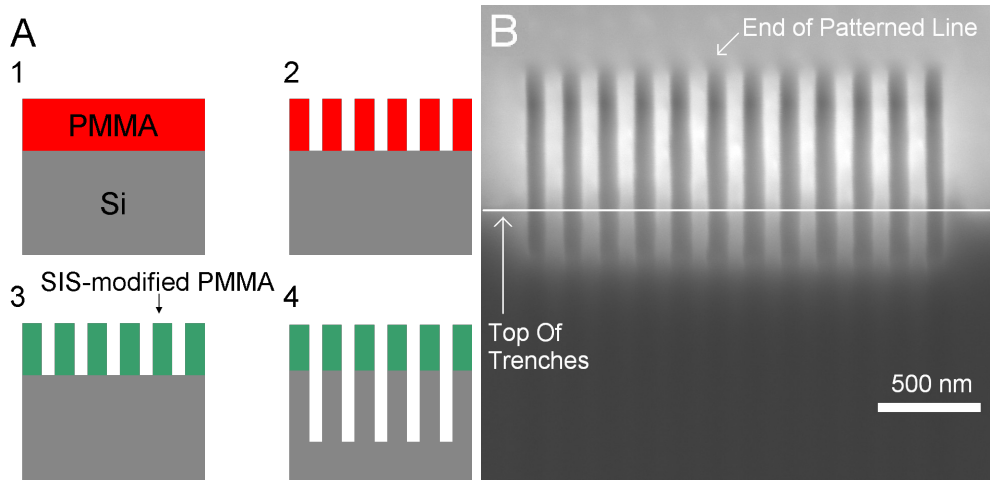
---

<sup>1</sup> D.A.Czaplewski, D.R. Tallant, G.A. Patrizi et al, J.Vac. Sc. Technol. B **27**, 581 (2009).

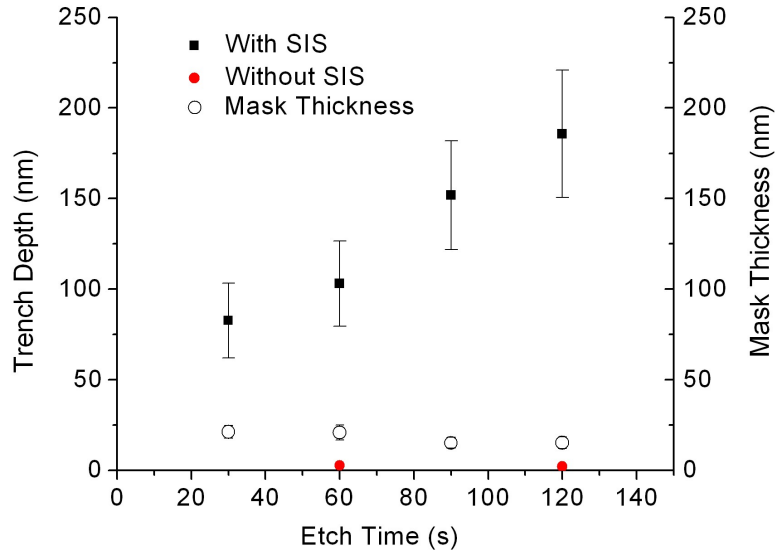
<sup>2</sup> Q. Peng, Y.C. Tseng, S.B. Darling and J. Elam, Adv. Mater. **22**, 5129 (2010).

<sup>3</sup> M. H. Somervell, D. S. Fryer, B. Osborn et al, J. Vac. Sci. Technol. B **18**, 2551 (2000).

<sup>4</sup> S. Mori, T. Morisawa, N. Matsuzawa et al, J. Vac. Sci. Technol. B **16**, 3739 (1998).



*Figure 1: A) Process sequence for using SIS-modified PMMA as an etch mask. 1. Spin-coat PMMA on Si substrate. 2. Exposure using electron beam lithography and development. 3. SIS using reaction with trimethyl aluminum and water. 4. Plasma etching in inductively-coupled plasma (ICP). B) Tilted (52°) cross-sectional SEM image of trenches etched in Si using SIS-modified PMMA as an etch mask. Trench dimensions: depth ~ 200nm, width ~90nm.*



*Figure 2: Depth of the trenches etched into Si as a function of the time of the silicon etching step. Closed dark squares: etched silicon trench depth using SIS-modified PMMA as mask. Closed red circles: trench depth without SIS. Open circles: thickness of the SIS-modified PMMA etch mask.*