Methylsilsesquioxane (MSQ) –A Novel Resist for Electron Beam Lithography

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The high contrast,[1] low line-edge roughness, and excellent mechanical stability and etch resistance of hydrogen silsesquioxane (HSQ) have made it one of the most widely-used resists for ultra-high-resolution electron beam lithography applications. Unfortunately, HSQ also exhibits behaviors that have complicated its widespread adoption as a general-purpose electron resist. These undesirable properties include, but are not limited to: low sensitivity, nonlinear development rates,[2] caustic aqueous-base developers that can attack certain substrates, and a currently-unexplained proximity effect not related to electron scattering.[3]

Here we show an alternative silsesquioxane, methylsilsesquioxane (MSQ) , may represent a solution to some or all of these issues. Like HSQ, MSQ is currently used as a flowable, low-k dielectric by the semiconductor industry,[4] and resembles HSQ at the molecular level-- in MSQ the Si-H bonds are replaced by Si-CH_3. The MSQ formulation used in these experiments was a high-molecular-weight resin with a low amount of residual silanol groups. The polymer was prepared using sol-gel condensation of a MTMS/TEOS mixture and the final ratio of Si-O to Si-CH_3 bonds were measured using NMR. Figure 1 shows MSQ structures with sub-20-nm features, fabricated using a Vistec VB300 100 keV e-beam tool and developed in several different solvents. Higher resolution may be accessible with alternative developers to overcome swelling and substrate adhesion issues. Base developers that were tested were found too aggressive (Fig. 2), which is attributed to a combination of base-induced etching and high molecular solubility due to remaining silanol groups.

Part of the exposure mechanism of MSQ is suggested by the Raman spectroscopy data in figure 2; electron exposure severs both the C-Si bond connecting the methyl groups to the cage and the C-H bonds holding the methyl groups themselves together. The resulting dangling bonds on the Si atoms can be passivated by the free hydrogen and form Si-H bonds. Cross-linking can occur through C-C and Si-O-Si. Since the Si-C bonds are more stable than the Si-H bonds in HSQ, MSQ may be less susceptible to the instabilities observed in HSQ. Experimental studies of these effects will be discussed.

While the resolution of MSQ is still not comparable to HSQ, these initial studies show resolution exceeding first results presented for HSQ. The understanding of exposure and development mechanism gained from the work herein will shed light on how to overcome the limitations of silsesquioxanes in general.

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[2] B. Cord, J. K. W. Yang, et al, J. Vac. Sci. Technol. B **27,** 2616 (2009).
[3] D. L. Olynick, J. A. Liddle, A. V. Tivanski, and M. K. Gilles, J. Vac. Sci. Technol. B **24,** 3048 (2006).
[4] W. Volksen, R. D. Miller, and G. Dubois, Chem. Rev. Online (2009).

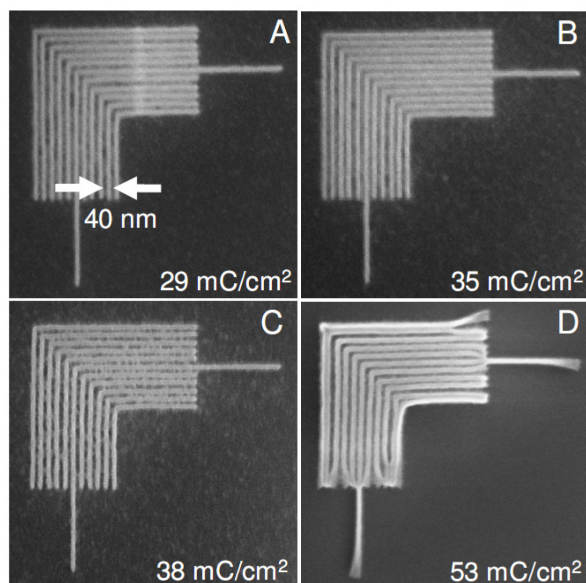

Figure 1: Scanning electron micrographs of “nested L” structures with a 40 nm pitch, fabricated in 20 nm of MSQ and developed for 30 s using glycol ether (A), methyl-iso-butyl-ketone (B), methanol (C), and 0.26N TMAH (D). A 5 nm layer of Transpin (a proprietary adhesion layer made by Molecular Imprints) was used under the resist to promote adhesion to the Si. Despite some swelling and bridging, all three structures developed in organic solvents (A-C) show clearly resolved ~20 nm dense and isolated features. The lines in (D) have resolved as well, but the aqueous-base developer has caused them to collapse and partially delaminate from the surface.

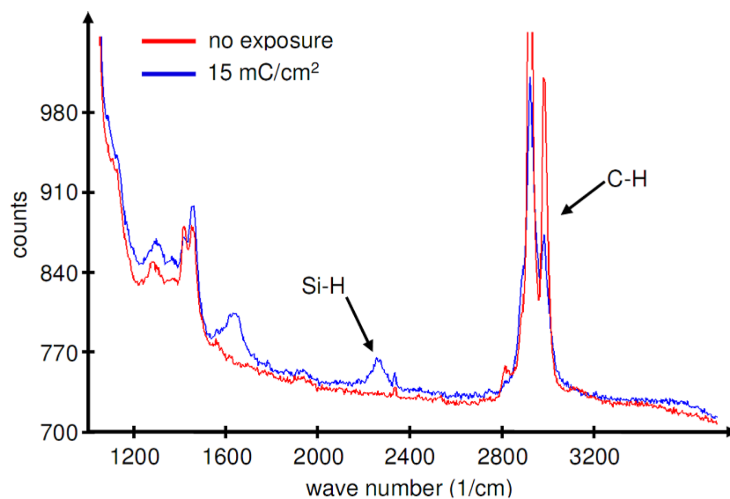

Figure 2: Raman spectra for MSQ before and after electron beam exposure. The two spectra show a sharp reduction in the C-H bond peak after exposure, suggesting that the incident electrons are disassembling the individual methyl groups. Similarly, the increase in Si-H bonds after exposure shows that the free hydrogen produced by the methyl-group destruction are able to combine with dangling Si bonds, which shows that the methyl groups are removed from the MSQ superstructure as well as destroyed.