Crosslinkable Photoacid Generators for Ultrahigh Loading in Epoxide Functionalized Molecular Resists

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Negative tone molecular resists based on the cationic polymerization of epoxides have shown promise for use in next generation lithography due chiefly to the ability of fully crosslinked features to resist pattern collapse during wet development at small length scales, and the high resolution enabled by the short lifetime of the photoacid (which is consumed upon initiating polymerization and is not regenerated without a chain-transfer-type reaction).

Because the photoacid lifetime is shorter than in traditional resist designs, resolution loss due to photoacid diffusion is less of a concern and should enable higher photoacid generator (PAG) loadings than is possible in conventional resists without reducing the resolution of the resist. This is important as higher PAG loadings can improve both sensitivity and PAG homogeneity/line-edge roughness. In one such epoxide functionalized resist (4Ep), the loading of a common onium salt PAG (TPS-SbF₆) could be increased from 5mol% up to 15mol% without affecting resolution and while improving sensitivity. The imaging quality of the lines were, however, greatly reduced. This was attributed to the inability of the PAG to participate in crosslinking causing it to act as a diluent to the crosslinked polymer network.

Functionalizing the PAG with groups that can participate in epoxide crosslinking should therefore allow for higher PAG loadings without inhibiting the resist's ability to form densely crosslinked features. To this end we developed a series of PAGs which were structurally analogous to TPS-SbF₆ (Figure 1) and were functionalized with groups that could participate in either epoxide-epoxide or phenol-epoxide crosslinking. We then evaluated the imaging performance of 4Ep under 100 keV electron-beam lithography at a variety of PAG loadings of both the functionalized and unfunctionalized PAGs.



Figure 1: Molecular structures of the resist (4Ep) and photoacid generator used in this study.



Figure 2: SEM micrograph of 100 keV electron-beam patterning of 4Ep with PEB of 90°C and 30 nm 1:1 L/S using (a) TPS-OH-SbF₆ at 55 mol% and (b) TPS-SbF₆ at 30 mol%