

# Phenol Functionalized Polymerization Control Additives for Negative Tone Cationic Molecular Resists

Hannah Narcross, Brandon Sharp

*School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332*

*hnarcross3@gatech.edu*

Clifford L. Henderson

*Department of Chemical and Biomedical Engineering, University of South Florida, Tampa, FL 33620*

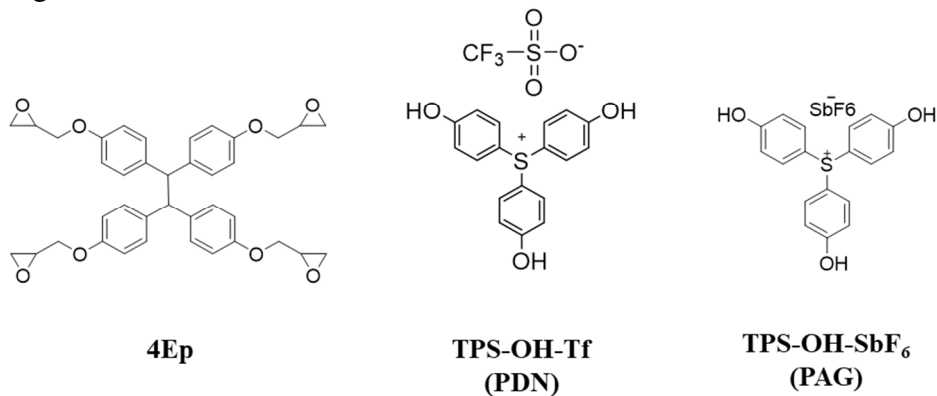
Negative tone molecular resists that image via the cationic polymerization of epoxides are promising materials for use with next generation lithography techniques due to their intrinsic advantages such as improved diffusion control and resistance to pattern collapse during solvent development. Since features are formed by the cationic polymerization of epoxides, controlling the rate and extent of crosslinking is critical to improving the ultimate resolution of these resists. The addition of base quenchers as are typically used in chemically amplified resists (CARs) is ineffective at altering the polymerization of these materials since the photoacid is not regenerated after initiating polymerization (without a chain-transfer-type reaction) and the chain-end has little reactivity towards bases. Previous work by our group has shown that photoacid generators (PAGs) containing weakly nucleophilic anions such as triflates act analogously to photodecomposable nucleophiles (PDNs) for these types of resists, as the triflate anion terminates chain propagation in unexposed regions but the triflic acid generated in exposed regions can act as an initiator or a chain-transfer agent.<sup>1</sup> Addition of a low percent of a TPS-Tf additive was shown to improve the ultimate resolution of a model epoxide resist (4Ep) by 5-10 nm, primarily by elimination of micro-bridging that is commonly seen in negative-tone resists.

We have further developed these triflate PDNs by functionalizing them with phenolic moieties which should provide even more control over crosslinking by 1) slowing the extent of crosslinking by acting as a chain-transfer agent and increasing the glass transition temperature of the resist and 2) allowing the incorporation of the PDN into the epoxide network via epoxide-phenol crosslinking, allowing the PDN to be used at higher loadings without decreasing the crosslink density of the patterned feature compared to a non-crosslinkable additive. The use of a phenol-functionalized hexafluoroantimonate PAG was also investigated as a PAG that could also be used at higher loadings while slowing the rate of crosslinking. It is hoped that by using both additives in tandem the

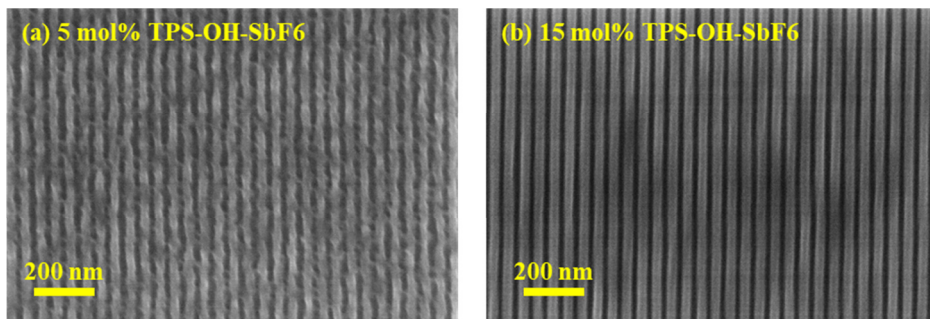
---

<sup>1</sup> Richard A. Lawson, Jun Sung Chun, Mark Neisser, Laren M. Tolbert, Clifford L. Henderson, "Methods of controlling cross-linking in negative-tone resists," Proc. SPIE 9051, Advances in Patterning Materials and Processes XXXI, 90510Q (27 March 2014)

ultimate resolution of 4Ep can be improved even further and that these compounds can act as general additives to improve the performance in all similar epoxide resists. Figure 2 shows initial E-Beam patterning of 4Ep using the phenol functionalized PAG which eliminates micro-bridging defects at higher loadings.



*Figure 1:* Molecular structure of the resist (4Ep) and functionalized additives used in this study.



*Figure 2:* SEM micrograph of 100 keV electron-beam patterning of 30 nm 1:1 L/S patterns using 4Ep and the phenol functionalized PAG TPS-OH-SbF<sub>6</sub> at (a) 5 mol% using a dose of 340  $\mu\text{C}/\text{cm}^2$  and (b) 15 mol% using a dose of 380  $\mu\text{C}/\text{cm}^2$ .