

Phenol-functionalized Polymerization Control Additives for Negative Tone Epoxide Crosslinking Molecular Resists

Running title: Phenol-functionalized Polymerization Control Additives

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Controlling undesired polymerization in nominally unexposed regions is critical to achieving high-resolution, defect-free patterns when using negative tone molecular resists based on the crosslinking of epoxides. Two onium salt additives, a photodecomposable nucleophile (PDN) and a photoacid generator (PAG), were functionalized with phenols in order to investigate their use as generalized additives capable of slowing crosslinking and improving the resolution of a variety of epoxide resists. Presented here are a phenol-functionalized PDN (TPS-OH-Tf) and a phenol-functionalized PAG (TPS-OH-SbF₆) used in combination with a model epoxide resist (4-Ep). Utilizing additives that contained phenols resulted in a decrease in resist sensitivity but enabled higher additive loadings which could be used to offset this loss in sensitivity. Using TPS-OH-SbF₆ did not provide enough polymerization control to prevent line broadening and the use of

TPS-OH-Tf was still required to achieve sub 35 nm 1:1 line:space patterns. Adding TPS-OH-Tf was also found to improve pattern collapse behavior at reduced (< 25 nm) feature sizes. Initial patterning using 100 keV electron-beam lithography showed that the resolution of 4-Ep was improved to 15 nm 1:1 line:space patterns using these phenol-functionalized additives, and demonstrate the potential of these additives to improve the resolution of a variety of epoxide crosslinking molecular resists.

I. INTRODUCTION

Maintaining Moore's law has presented the semiconductor industry with significant scaling challenges in both lithographic processes and materials, especially as features approach molecular and atomic length scales. Next generation lithography (NGL) techniques such as ion beam, electron-beam (e-beam) and extreme ultraviolet (EUV) lithography have shown promise for use in sub-10 nm patterning, but the traditionally used polymeric chemically amplified resists suffer from significant patterning issues at these feature sizes including resolution loss due to photoacid diffusion, high line edge roughness, and pattern collapse during post wet-development drying. Significant research has been dedicated to finding alternative resist chemistries and materials which are capable of patterning at these length scales. Chemically amplified molecular resists have been investigated in the hopes that their small size and narrow molecular weight distribution can provide improved resolution, line edge roughness (LER), and a more homogenous distribution of photoacid generator (PAG) throughout the resist.¹⁻⁴ Negative tone molecular resists based on the polymerization of

groups such as epoxides are of particular interest as the fully crosslinked features have been demonstrated to be more resistant to pattern collapse and potential control of photoacid blur.⁵

Our group has extensively investigated one such resist, TPOE-4Ep (4-Ep), which showed promising results but was resolution limited to 35 nm half-pitch lines due to line-broadening caused by the spread of polymerization into unexposed regions.⁶

Traditionally base quenchers are used to improve resolution by quenching photoacids that diffuse outside of exposed regions, but these additives proved ineffective in 4-Ep due to the difference in imaging mechanism.⁷ In resists based on the cationic polymerization of epoxides, photoacids have short lifetimes before initiating polymerization (without being regenerated) and base quenchers are incapable of terminating polymerization in exposed regions. In order to improve the performance of any resists of this type, it is therefore critical to control the rate and extent of crosslinking.

One method of controlling crosslinking previously explored was the use of a photodecomposable nucleophile (PDN) additive that quenched polymerization in unexposed regions but could transfer or (to a lesser extent) initiate polymerization in exposed regions (FIG. 1).⁷ The use of these materials has been demonstrated to dramatically improve the resolution of epoxide-based materials, improving the resolution of 4-Ep to 19 nm half-pitch. Another method investigated was the introduction of phenolic groups onto the resist molecule which controls crosslinking by introducing a new reaction pathway (FIG. 2) and raising the glass transition temperature (T_g) of the resist.⁷⁻⁹ Both methods were promising, but required either the use of an additive which

cannot be crosslinked into the network (limiting the amount that can be added before diluting the crosslink density of the network) or structural modification of the resist itself.

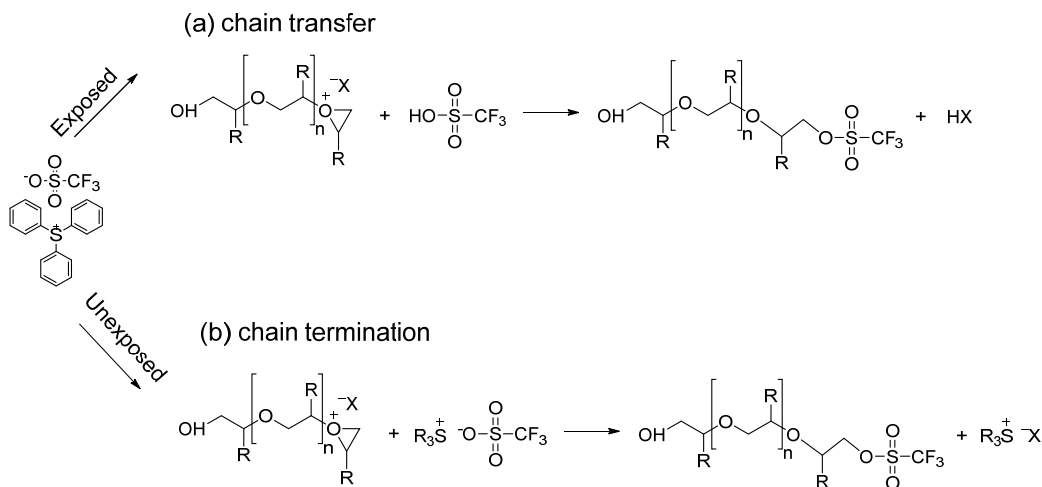


FIG. 1. Possible reaction pathways of epoxide crosslinking in the presence of an onium triflate PDN in both unexposed and exposed regions.

In order to further probe the ultimate resolution of negative-tone epoxide crosslinkable resists, it would be therefore useful to have a set of generalized PDN and PAG additives functionalized with phenolic groups that could be blended into any epoxide crosslinkable resist in order to provide improved polymerization control and improve resolution without requiring structural modification of the resist itself. Previous results also suggest that phenol-functionalization should also allow for higher loadings of either additive to be used without diluting the crosslink density of the resist.¹⁰ Phenol-functionalized PAGs might also provide enough intrinsic polymerization control in unexposed regions to eliminate the need for a PDN to achieve high resolution patterning.

To that end, both a PDN and a PAG were functionalized with phenolic groups (FIG. 3) with the expectation that both additives could be used to improve the resolution

of a model epoxide resist (4-Ep) by slowing the rate of crosslinking, increasing the film T_g , terminating polymerization in unexposed regions, and could both be used at higher overall additive loadings than their unfunctionalized analogues.

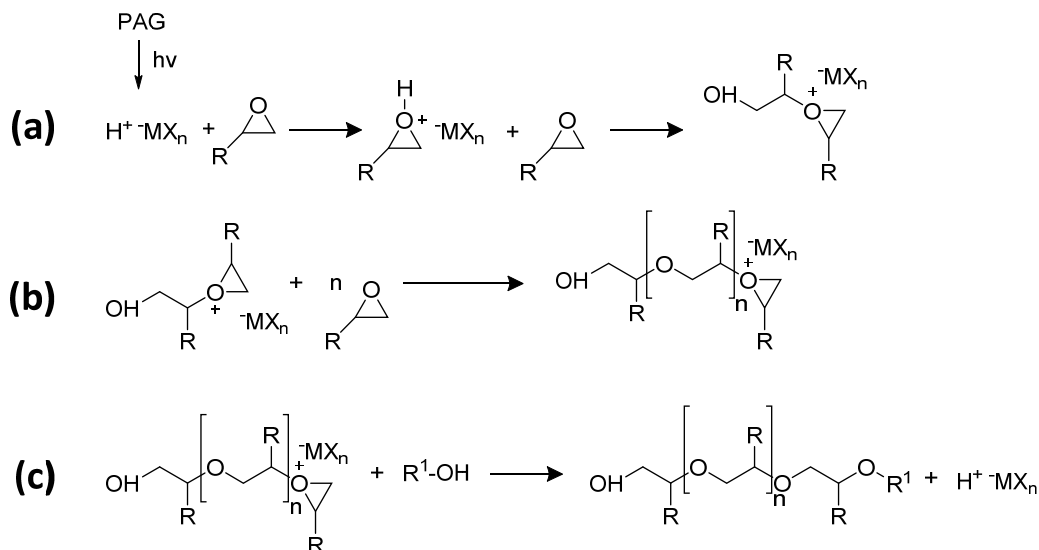


FIG. 2. Potential crosslinking mechanisms following initiation (a) of either epoxide-epoxide crosslinking (b) or epoxide-phenol crosslinking (c).

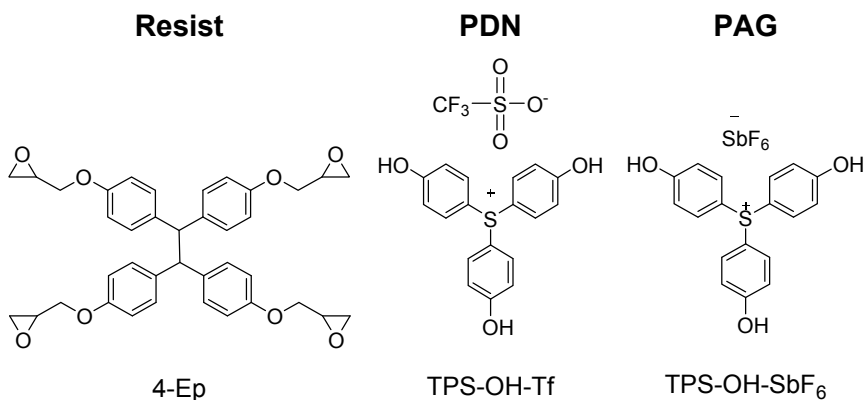


FIG. 3. Structures of the resist (4-Ep) and functionalized additives investigated in this study.

II. EXPERIMENTAL

A. Synthesis

All reagents unless otherwise noted were purchased from TCI America or Sigma-Aldrich and used without further purification. Tris(4-hydroxyphenyl)sulfonium chloride (TPS-OH-Cl) was synthesized using modified procedure described by Crivello and Lam.¹¹ Metathesis with either sodium triflate or sodium antimonate was then carried out by adding TPS-OH-Cl and an equimolar amount of a sodium salt with the desired anion to a vial containing acetone and a slight amount of water. The solution was stirred vigorously overnight at room temperature. Precipitated solids were then filtered out of solution, re-dissolved in ethyl acetate, and washed three times with distilled water to remove any remaining sodium salts. Solvent was removed with a rotary evaporator and the salts were dried overnight in a vacuum oven. The anion of both tris(4-hydroxyphenyl)sulfonium triflate (TPS-OH-Tf) and tris(4-hydroxyphenyl)sulfonium antimonate (TPS-OH-SbF₆) were confirmed via electrospray ionization mass spectrometry.

B. Lithographic Evaluation

Solutions with 2 wt. % of 4-Ep, TPS-OH-Tf, and TPS-OH-SbF₆ in ethyl lactate were prepared and blended together at various ratios to obtain a series of solutions with the desired mol. % of PDN (TPS-OH-Tf) and PAG (TPS-OH-SbF₆). Each solution was cast onto silicon wafers pieces (ordered from University Wafer and cleaned with oxygen plasma immediately prior to use) by spin-coating at 2000 rpm. All wafers were subjected to a post-apply bake (PAB) at 60 °C for 2 min and a 90 °C post-exposure bake for 1 min. This was followed by development in methyl isobutyl ketone (MIBK) for 30 s and a 10 s rinse with isopropyl alcohol. Deep Ultraviolet (DUV) exposures were performed with an Oriel Instruments 500 W Hg-Xe arc lamp using a 248 nm bandpass filter, and the

resulting film thicknesses were measured using a M-2000 Woolam Ellipsometer. Film thickness measurements collected using the ellipsometer were also used to calculate the glass transition temperatures of different resist blends cast as thin films using a method described previously.¹² E-beam exposures and patterning were performed with a JEOL JBX-9300FS electron beam lithography system, using an acceleration voltage of 100-keV and a current of 100-pA. Film thicknesses for e-beam contrast curves were measured using a Tencor KLA P15 Profilometer. E-beam patterns were imaged using a Carl Zeiss Ultra 60 scanning electron microscope (SEM) with a 2 keV acceleration voltage.

III. RESULTS AND DISCUSSION

A. Effect of Phenol Functionalization

DUV contrast curves of 4-Ep were collected with 5 mol. % of either TPS-SbF₆ or TPS-OH-SbF₆ as a PAG and TPS-Tf or TPS-OH-Tf as a PDN to investigate how the addition of phenols on the additives affected crosslinking behavior (FIG. 4). Resist blends containing the functionalized additives showed a shift in E₁ (the exposure dose at which the normalized remaining film thickness or NRT is 1) away from 0 mJ/cm² which is consistent with the predicted effect of the phenols slowing or controlling crosslinking.

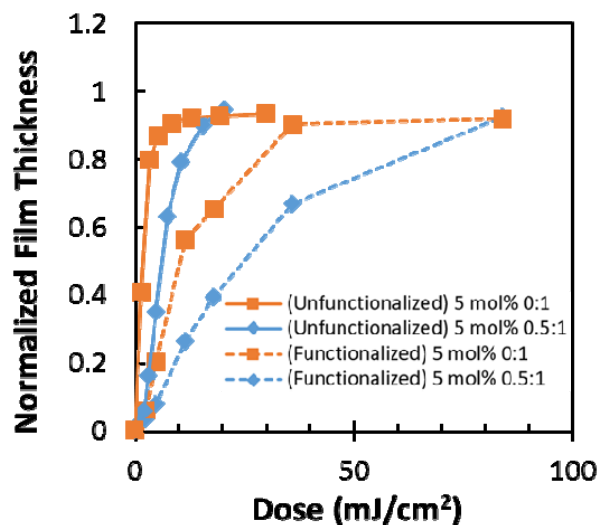


FIG. 4. (Color online) DUV contrast curves showing differences in 4-Ep behavior when using 5 mol. % of the phenol-functionalized or unfunctionalized PAG. Amounts of PDN added are reported as a molar ratio relative to PAG (PDN:PAG).

Since one of the proposed methods by which phenols could control crosslinking was by increasing the glass transition temperature of the film, the T_g of 4-Ep films blended with different amounts of the phenol-functionalized PAG was determined using ellipsometry (FIG. 5) It was found that in fact the T_g of the film was not dramatically affected at the additive loadings investigated in this study. At the highest total additive loading investigated (30 mol. % additive) the measured film T_g was only increased by 3 °C, which is unlikely to significantly affect the mobility of the active chain ends in the un-crosslinked or crosslinked resist. The sensitivity shift can therefore be attributed primarily to a decrease in the rate of cross-linking caused by the introduction of the new epoxide-phenol crosslinking mechanism.

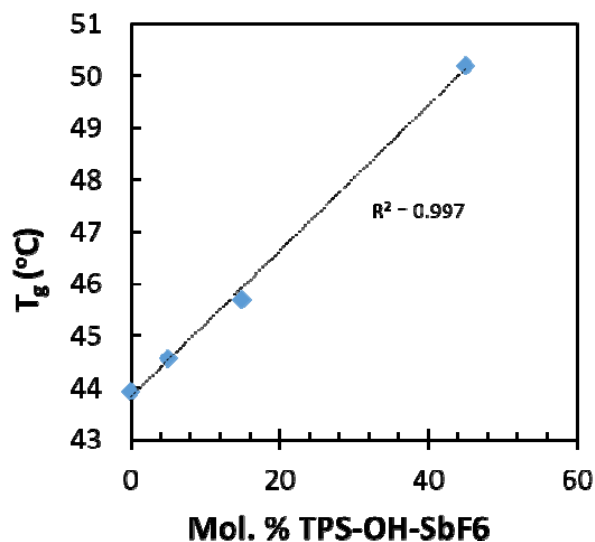


FIG. 5. The measured thin film T_g of 4-Ep as a function of mol. % phenol-functionalized PAG.

Contrast curves collected using a higher energy 100 keV e-beam source also showed a decrease in sensitivity when using the functionalized PAG, albeit a much greater one than was observed in resists exposed using DUV (FIG. 6). Additionally, the extent of crosslinking (which is correlated to NRT), decreased when using e-beam but not DUV. Both results can be related back to the differences in the primary method of acid generation between the two exposure sources; under DUV it is the direct excitation of the PAG by DUV photons whereas under e-beam it is PAG excitation via secondary electron transfer from the resist material. Previous research has demonstrated that PAG electron affinity has good correlation with acid generation efficiency under high energy exposure sources, as PAGs with high electron affinities can more efficiently capture secondary electrons.¹³ Further research by Tagawa and colleagues found that the incorporation of electron withdrawing groups onto the aromatic rings in sulfonium salt PAGs increased their electron affinity; therefore it is reasonable to assume that the incorporation of the

electron donating phenolic groups could decrease its electron affinity.^{14, 15} This would explain why both the extent of crosslinking and sensitivity of 4-Ep blends with phenol-functionalized PAG are much poorer than those with unfunctionalized PAG at identical mol. % when using e-beam compared to DUV, since not only is the rate of crosslinking decreased but also the acid generation efficiency of the PAG itself.

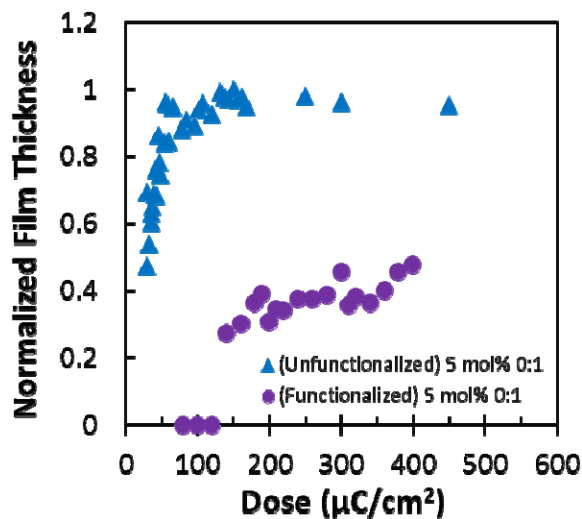


FIG. 6. (Color online) 100 keV e-beam contrast curves of 4-Ep using 5 mol. % of either the phenol-functionalized or unfunctionalized PAG.

B. Loading Effects

Our group has previously determined that when using epoxide-crosslinkable molecular resists, increasing the amount of PAG beyond a certain mol. % can result in a loss of sensitivity if the PAG cannot crosslink with the resist material (illustrated here in FIG. 8d).¹⁰ Since it was also demonstrated that 4-Ep blends with TPS-OH-SbF₆ can achieve an NRT of 1 using PAG loadings up to 50 mol. %, the performance of 4-Ep using different amounts of added PDN was investigated at typical (5 mol. %) and elevated (15 mol. %) PAG loadings. It was hoped that some of the sensitivity loss

inherent to using these phenol-functionalized additives could be offset by increasing the PAG loading while still retaining the crosslinking control enabled by the addition of phenols and PDN.

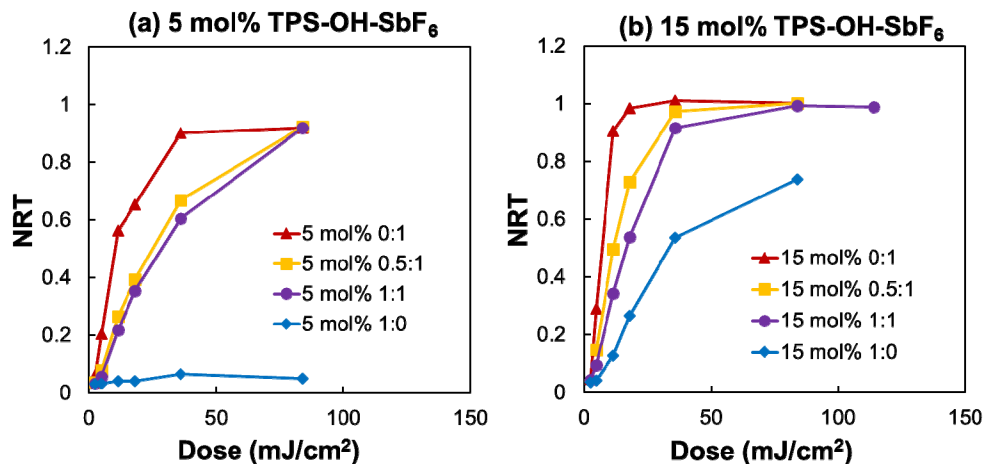


FIG. 7. (Color online) DUV contrast curves of 4-Ep at 5 mol. % (a) or 15 mol. % (b) of the phenol-functionalized PAG and different amounts of the phenol-functionalized PDN reported as a molar ratio relative to the amount of PAG (PDN:PAG).

Contrast curves collected using 248 nm DUV light can be seen in FIG. 7 which show expected behavior; increasing the amount of PDN causes a decrease in sensitivity, and increasing the PAG loading from 5 mol. % to 15 mol.% improved the sensitivity at all PDN:PAG ratios. Similar behaviors were observed in e-beam contrast curves with the exception that at 5 mol. % PAG there was not a clear trend in the effect of the addition of PDN on sensitivity.

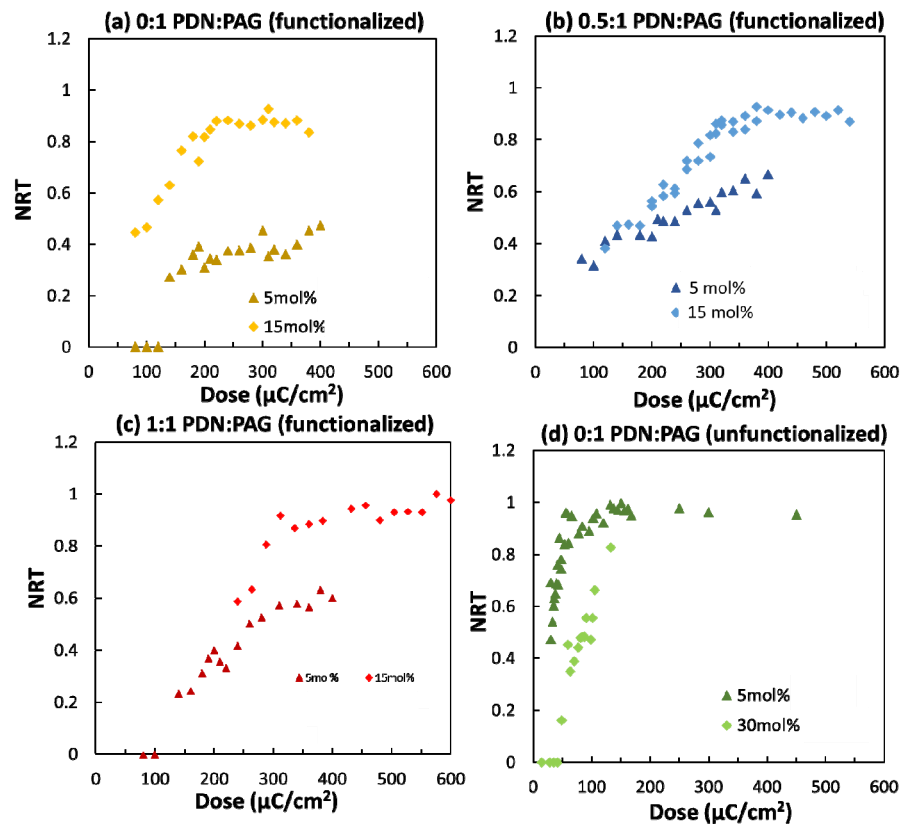


FIG. 8. (Color online) 100 keV e-beam contrast curves of 4-Ep using 5 or 15 mol. % phenol-functionalized PAG using PDN:PAG molar ratios of 0:1 (a) 0.5:1 (b) or 1:1 (c). A contrast curve of 4-Ep using 5 or 30 mol. % unfunctionalized PAG can be seen in (d).

C. E-beam Patterning

Initial 30 nm 1:1 (line:space) patterns were used to compare the imaging performance of 4-Ep at a variety of functionalized PAG and PDN loadings (FIG. 9). Despite being under-dosed, bridging defects were observed at 5 mol. % PAG. These defects were eliminated by increasing the PAG loading to 15 mol. %. This was probably due to a combination of the increased crosslink density (higher NRT) as well as the increased amount of phenols in the resist which provide more polymerization control in unexposed regions. Bridging defects were also eliminated in the formulations that

included PDN additives, despite little-to-no improvement in the degree of crosslinking (NRT remained roughly the same), illustrating the polymerization control that a PDN provides. Line broadening, which was attributed to the propagation of polymerization outside of nominally exposed regions, was observed at both 0:1 and 0.5:1 PDN:PAG. At 1:1 PDN:PAG, lines appear to successfully image at the correct line widths, but some of this could also be attributed to this pattern being potentially underdosed. This suggests that simply functionalizing the PAG with phenolic groups does not provide enough polymerization control to achieve feature sizes at or below 30 nm and that PDN is still required.

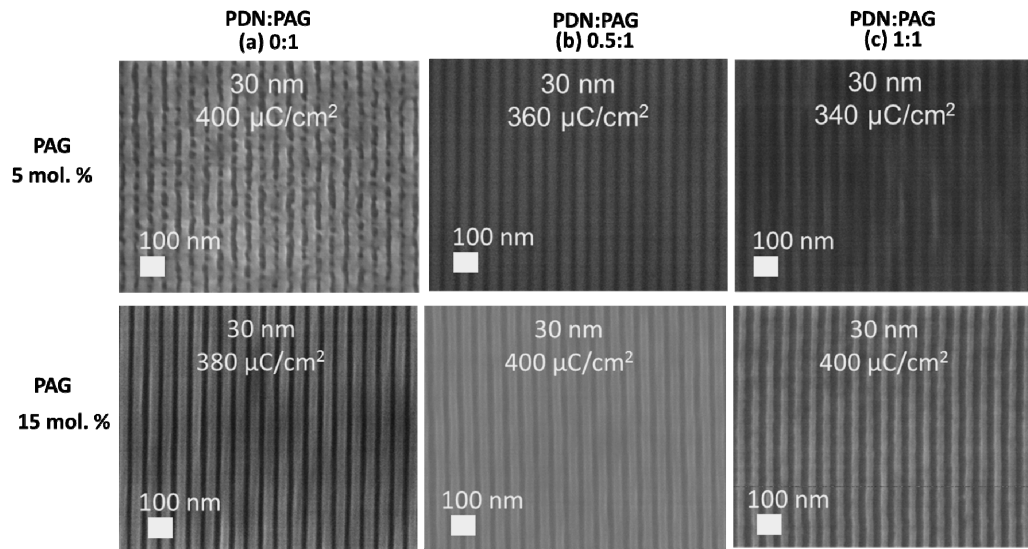


FIG. 9. Comparison of 30 nm line:space patterns imaged using 5 or 15 mol. % TPS-OH-SbF₆ and varying amounts of TPS-OH-Tf, reported as a molar ratio of PDN to PAG (PDN:PAG).

Since 4-Ep blends formulated with 5 mol. % PAG did not achieve an NRT of 1 at any of the doses investigated, resist blends using 15 mol. % PAG were chosen for further patterning studies to investigate their ultimate resolution (FIG. 10). Resist formulations

without PDN successfully imaged 25 nm lines, but patterns at 20 nm and below failed due to pattern collapse. Features down to 15 nm resolved when using 0.5:1 PDN:PAG with no pattern collapse or bridging defects. It is interesting that pattern collapse was mitigated simply through the addition of PDN. Previous work by Crivello and Ortiz reported that phenols could be used to increase the extent of conversion of the photoinitiated polymerization of epoxides as the chain-transfer mechanism mobilized the propagating species which would otherwise be trapped in the glassy matrix of the crosslinked network.¹⁶ This could explain the observed results, as a higher extent of conversion granted by the added phenols on the PDN would likely increase the mechanical modulus of the patterned feature and thus its resistance to pattern collapse. If this is in fact the explanation for the change in behavior, then phenol-functionalized additives can potentially be used to simultaneously improve pattern collapse and resolution in epoxide molecular resists.

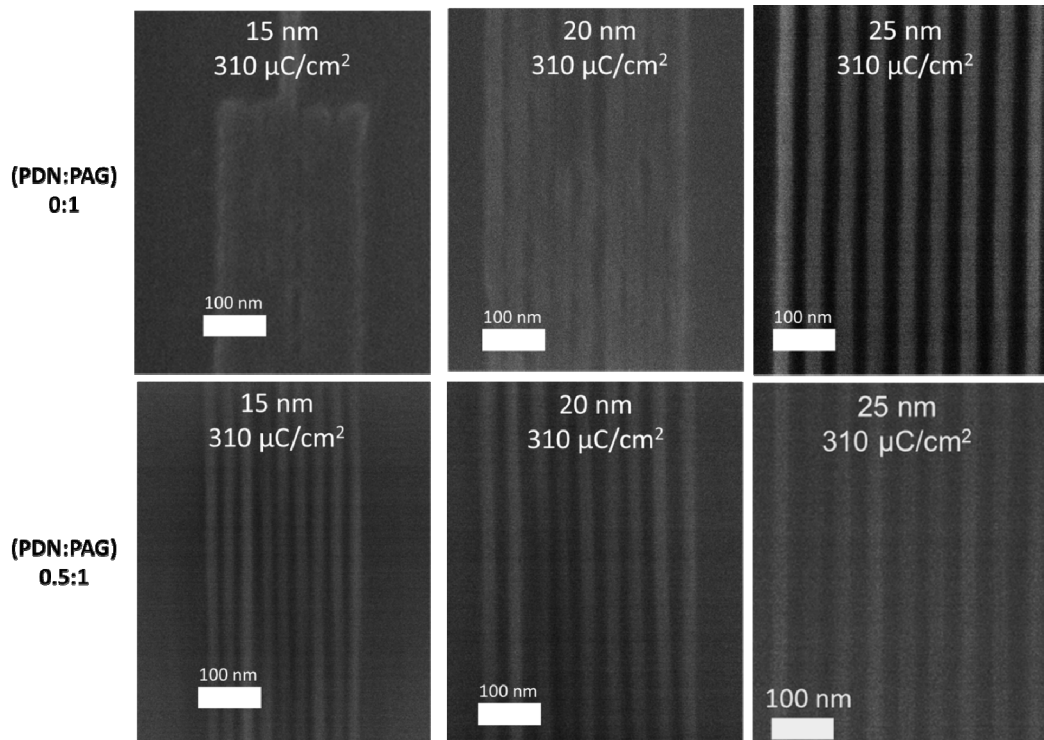


FIG. 10. High resolution 1:1 (line:space) patterns of 4-Ep using 15 mol. % PAG exposed via 100 keV e-beam lithography.

IV. SUMMARY AND CONCLUSIONS

Two additives used in chemically amplified molecular resists based on the crosslinking of epoxides, a PAG and a PDN, were functionalized with phenolic groups in the expectation that they would improve the resolution of a model epoxide resist by slowing the rate of crosslinking via the introduction of a new polymerization pathway, increasing the film T_g , terminating polymerization in unexposed regions, and could both be used at much higher overall additive loadings than their unfunctionalized analogues. It was found that introducing phenolic groups onto the PAG/PDN decreased resist sensitivity, but allowed for higher overall additive loadings to be used which could be used to improve sensitivity. Phenol-functionalized additives were not found to significantly affect the T_g of the resist at the loadings investigated, and the loss of sensitivity was attributed to the addition of the additional phenol-epoxide crosslinking mechanism slowing the overall rate of crosslinking. Simply functionalizing the PAG with phenolic groups did not provide enough polymerization control to resolve 30 nm lines at typical (5 mol. %) or elevated (15 mol. %) PAG loadings and PDN was required to prevent line broadening. The addition of PDN was also shown to improve pattern collapse behavior which was attributed to a greater extent of conversion/crosslinking in the resist. Initial e-beam patterning results indicate that the resolution of 4-Ep was improved to 15 nm dense features using these phenol-functionalized additives.

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