

Advancing the Sequence-defined Polypeptoid EUV Resist Platform: Multi-site Decarboxylation and Metal Sensitization

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Primary CNF Tools Used: JEOL JBX-6300FS E-beam Lithography System, JEOL JBX-9500FS E-beam Lithography System, ASML DUV Stepper, AFM - Veeco Icon, Zeiss Gemini SEM, J.A. Woollam RC2 Spectroscopic Ellipsometer

Abstract:

Our sequence-defined polypeptoids function as single-component, PAG-free negative-tone resists under EUV and electron-beam (e-beam) exposure, with patterning driven by decarboxylation of the peptoid chain by loss of carboxylic acid ($-\text{COOH}$) groups. In the original system, a single C-terminal $-\text{COOH}$ per chain, a serendipitous byproduct of solid-phase submonomer synthesis, served as the solubility-switch group, and the fully organic composition limited absorption at EUV wavelength. This year we extended the platform along two directions. First, sequence-controlled synthesis was used to install multiple $-\text{COOH}$ groups at defined positions along the chain, transforming the $-\text{COOH}$ from a synthesis byproduct into rationally placed solubility-switch sites. Residual gas analysis of five multi- $-\text{COOH}$ decamer sequences under EUV exposure revealed that the nominally "inactive" aromatic side groups (phenyl versus phenol) substantially modulate decarboxylation, and that $-\text{COOH}$ groups at the C-terminal, mid-chain, and N-terminal positions react with distinct efficiencies. Second, high-Z metal elements were incorporated by strategies including physical blending of metal salts, and a sequence-controlled chelation strategy in which 8-hydroxyquinoline submonomers coordinate Zn(II) or Sn(II) into dimeric metal-peptoid complexes. EUV reflectometry confirmed the expected enhancement in linear attenuation, with the magnitude trending with the atomic photoabsorption cross-section of the bound metal. Together, these directions yield a set of design rules for next generation of polypeptoid EUV resists.

Summary of Research:

Our previous studies indicated that the molecular homogeneity of the polypeptoid platform means that the loss of a single functional group per chain produces a detectable, uniform solubility contrast, and that every

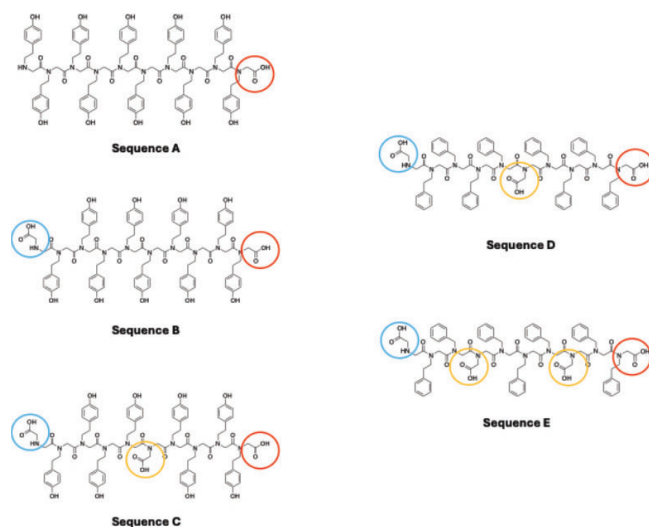


Figure 1: Molecular structures of the five multi- $-\text{COOH}$ decamer polypeptoid sequences (A-E). Sequences A-C bear phenol side groups and Sequences D-E bear phenyl side groups; each carries one to four $-\text{COOH}$ groups distributed across the C-terminal (red), N-terminal (blue), and mid-chain (yellow) positions.

chain in the film is structurally identical, making the resist not only a candidate material but also an unusually clean model system for studying resist patterning chemistry [1]. Building on this, we placed $-\text{COOH}$ groups at chosen positions along the chain (Figure 1). Five decamer sequences (A-E) were synthesized, carrying one to four $-\text{COOH}$ groups distributed across C-terminal, N-terminal, and mid-chain positions, and built with either phenol (A-C) or phenyl (D-E) aromatic side groups. Because decarboxylation releases CO_2 , residual gas analysis (RGA) during EUV exposure provides a direct probe of the reaction, monitored through the CO_2 signal at m/z 44 (Figure 2).

Two findings emerged. First, the phenyl-containing sequences outgassed nearly an order of magnitude more CO_2 than their phenol-containing counterparts. A direct comparison of Sequences C and D, which differ only by the phenol hydroxyl, isolates this effect from

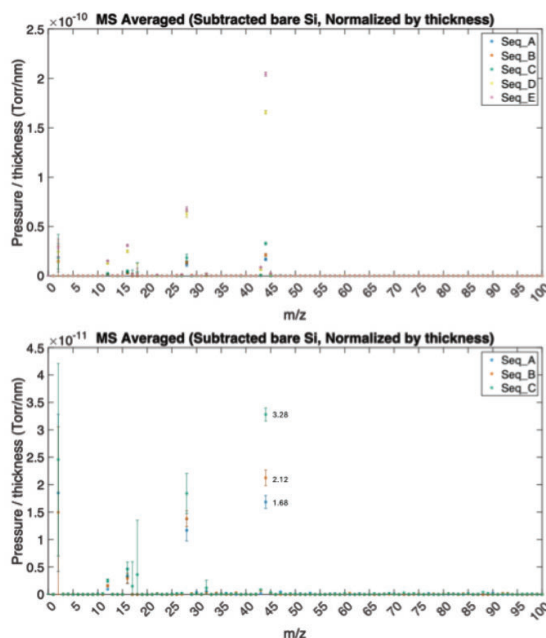


Figure 2: Thickness-normalized RGA mass spectra of outgassed species from Sequences A-E (Top) and A-C (bottom, zoomed-in) under EUV exposure.

compositional differences and points to the phenolic -OH as the likely source of suppression, plausibly through competing radical or electron/hole scavenging pathways. Second, the three types of -COOH groups decarboxylate with distinct efficiencies, in the approximate order C-terminal > mid-chain > N-terminal, as the thickness-normalized CO_2 signals across the sequences do not follow a simple stoichiometric ratio. Preliminary e-beam patterning, used here as a proxy for EUV, confirmed that these multi-COOH sequences are patternable (Figure 3), with development conditions tailored to the hydrophilicity of each sequence.

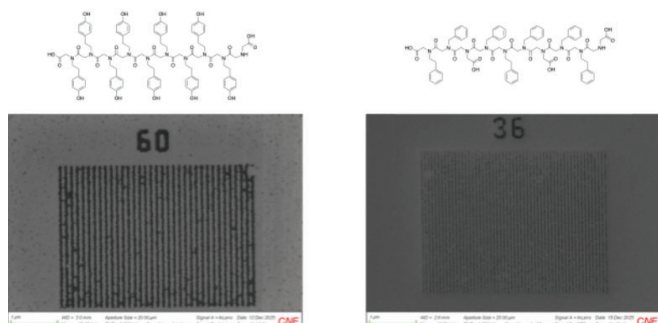


Figure 3: Preliminary e-beam patterning results from Sequences B (left) and E (right), demonstrating the patternability of multi-COOH polypeptoid sequences under e-beam exposure.

To raise EUV absorption beyond the low cross-sections of C, H, O, and N, high-Z elements were incorporated by two strategies [2]. Physical blending of ZnCl_2 with a tyramine-based hexamer at a 1 Zn : 2 -COOH ratio increased e-beam sensitivity, lowering the dose required

to pattern, as a proof of concept, though at the cost of reduced resolution and post-development surface residues, and with no control over metal placement. A sequence-controlled route was then developed using an 8-hydroxyquinoline (8-HQ) submonomer [3], a strong bidentate chelator, installed at a defined chain position. UV-Vis titration confirmed formation of $\text{M}(8\text{-HQ})_2$ complexes with $\text{Zn}(\text{II})$ or $\text{Sn}(\text{II})$, saturating at a 1:2 metal-to-peptoid ratio, which couples two chains through a single shared metal center into a dimeric architecture with the metal fixed at a sequence-defined position. EUV reflectometry at the Center for X-ray Optics (LBNL) confirmed the intended enhancement [4]: the linear attenuation coefficient at 13.5 nm rose from $4.744 \mu\text{m}^{-1}$ for the metal-free reference to $5.117 \mu\text{m}^{-1}$ for the Zn-peptoid and $5.396 \mu\text{m}^{-1}$ for the Sn-peptoid, in the order expected from the atomic photoabsorption cross-sections of the bound metals.

Conclusions and Future Steps:

These two directions extend the polypeptoid resist platform along chemistry (the number and location of reactive decarboxylation sites) and elemental composition (the placement of high-Z atoms at sequence-defined positions), while preserving the molecular precision that distinguishes it from conventional polymeric resists. Treated as model systems, they yield design rules for next-generation polypeptoid resists: which chain positions decarboxylate most efficiently, how nominally inactive side groups modulate that chemistry, and how metals can be localized at defined sites. Future work will combine sequence-defined decarboxylation sites and metal-binding sites within a single chain, and scale metal loading by installing multiple 8-HQ units to further amplify EUV absorption.

References:

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