Design and Synthesis of Sequence-Defined Oligopeptoids for Potential Lithographic Use

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Primary CNF Tools Used: AFM-Veeco Icon, ASML PAS 5500/300C DUV Wafer Stepper, and Woollam RC2 Spectroscopic Ellipsometer.

Abstract:

Extreme-ultraviolet (EUV) lithography underpins continued device miniaturization, yet conventional photoresists suffer from stochastic issues and the resolution-sensitivity-roughness trade-off at sub-10 nm dimensions.1, 2 Herein, we present a modular synthetic platform based on sequence-defined peptoids to overcome these limitations. In this work, two distinct oligopeptoid architectures were explored. The first employs a chemical amplification mechanism, using Boc-protected side chains to trigger solubility switching upon acid-catalyzed deprotection.3 Their lithographic performance, using either ionic or non-ionic photoacid generators (PAGs), was evaluated under deep-ultraviolet (DUV) exposure. The second is a creative innovation in which non-ionic PAGs were covalently tethered onto peptoid backbones via copper-catalyzed azide-alkyne cycloaddition, making the PAG itself the solubility-switch moiety and ensuring uniform acid distribution.

Summary of Research:

We designed and synthesized bioinspired, sequence-defined and length-controlled oligopeptoids incorporating both clickable sites and solubility-switch functional groups. Two distinct strategies were explored: one employing Boc-protected tyramines as acid-labile switches in a chemically amplified resist system, and the other utilizing tethered non-ionic PAGs directly integrated into the peptoid backbone.

Thermal stability studies of both the oligopeptoids and PAG components helped determining the suitable post-apply and post-exposure bake temperatures. Through systematic evaluation of key lithographic parameters—including developer composition, TMAH dilution ratios, and film thickness—a set of processing parameters was established to generate discernible patterns under DUV exposure. Intriguingly, a tone-switch behavior was observed in peptoid films formulated with ionic PAGs, wherein thinner films behaved as positive-tone resists while thicker films as negative-tone, highlighting the complex interplay between film morphology and development responses.

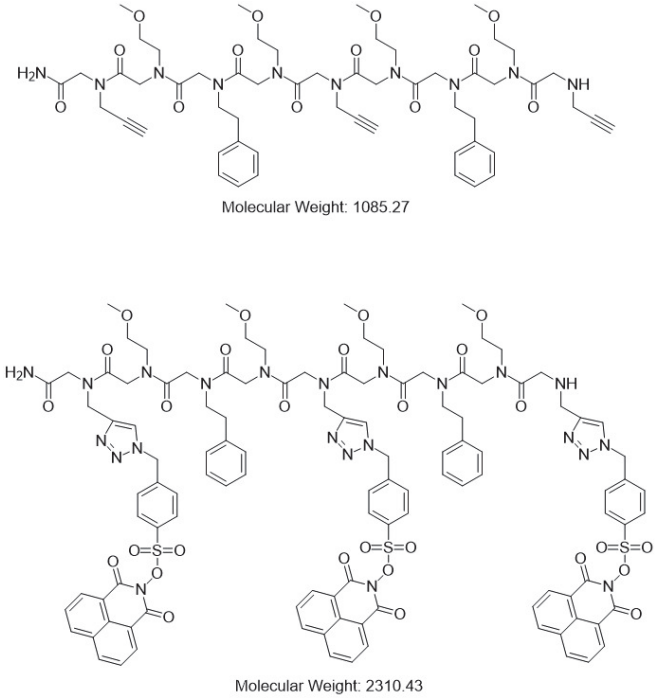

Figure 1: (a) Peptoid structure of PMFMPMFMP 9-mer, designed with propagyl amines as potential sties of click reaction and (b) PAG-incorporated peptoid by click reaction.

Furthermore, a brand new type of resist using tethered PAG as the solubility switch was invented. The CuAAC click reaction was used to tether azide-functionalized PAGs onto peptoid backbones, with LC-MS confirming efficient tri-site conjugation under optimized reaction

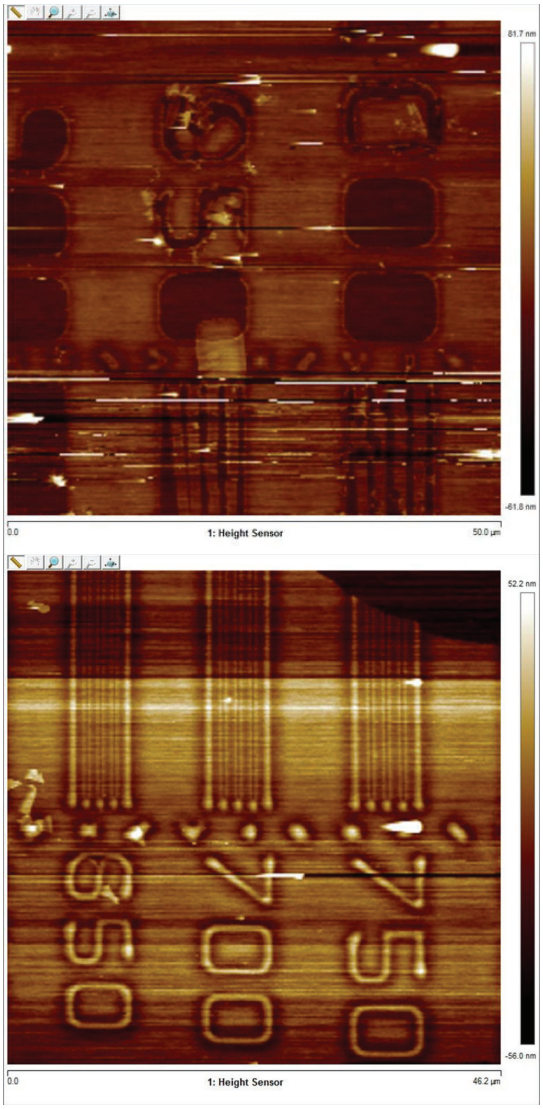

Figure 2: DUV (248 nm) 1:1 Line space pattern; dose 60 mJ/cm2; post-apply and post-exposure bake temperature 110 ˚C; 40 wt.% TPS-TF, developed in (a) undiluted AZ 726 for 3 seconds and (b) 50× diluted AZ 726 for 45 seconds, observed under AFM.

conditions. Comparative evaluation of purification methods revealed that bypassing the alumina column step significantly improved overall yield particularly due to the low amount of copper catalyst content.

Overall, this study demonstrates a modular synthetic framework for peptoid-based photoresists with tunable chemical functionality and processibility, paving the way for further investigations into their performance under EUV and electron beam lithographic conditions, advancing the development of next-generation organic resist materials.

References:

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