Sequence-Defined Polypeptoids Enable Stochastics Control and Discovery of Novel Patterning Mechanism in Next-Generation EUV Resists

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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

Abstract:

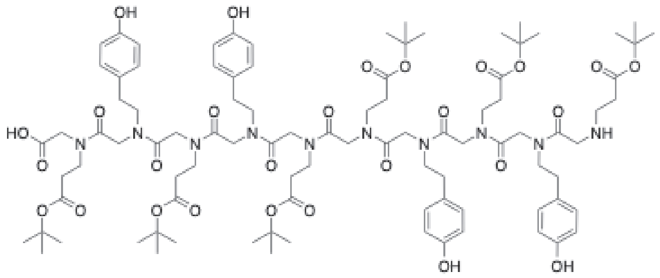
As lithography continues to advance into the extreme ultraviolet (EUV) regime, stochastic effects are becoming an increasingly significant challenge. One key contributor to it is the chemical stochastics, which arises from molecular-level inhomogeneities within photoresist materials. Traditional polymer-based photoresists often exhibit variations in molecular weight, composition, and sequence. In the case of chemically amplified resists (CARs), unbound photoacid generator (PAG) molecules may distribute unevenly at the nanoscale, and the lateral acid diffusion after exposure are somehow uncontrolled, further adding to stochastics. In this project, we investigated a photoresist system built on sequence-defined polypeptoids, which can be precisely tailored in terms of length, composition, and sequence, using the solid-phase submonomer synthesis method. These polypeptoid resists can be patterned in negative tone using either electron beam or EUV exposure, without requiring any additional photoactive components. This results in a monomolecular resist formulation that greatly minimizes chemical stochastic effects. We explored the patterning mechanism through a variety of characterization techniques and propose that the solubility behavior is driven by a mechanism that is rarely considered in EUV photoresist design. Additionally, we investigated how variations in composition and sequence affect lithographic performance, revealing consistent trends. With EUV exposure, we achieved a resolution of 14 nm half-pitch.

Summary of Research:

We have developed a novel sequence-defined polypeptoid photoresist platform to address stochastics challenges in EUV lithography. Traditional polymeric photoresists struggle with chemical stochastics originating from the random nature of conventional polymers in terms of molecular weight, composition and sequence, as well as the random distribution of photoactive compounds and lateral acid diffusion in terms of CARs. There are also environmental concerns due to the use of PAGs which are mostly fluorinated compounds [1]. The new polypeptoid photoresist system, synthesized via solid-phase submonomer synthesis, features precisely positioned functional groups and exhibits uniform chain length, composition, and sequence [2-3]. These materials exhibit ultra-low dispersity and tunable properties, enabling intrinsic patternability under EUV and e-beam exposures without the need for PAGs. Their unique decarboxylation-based mechanism allows for high-resolution patterning (down to 14 nm half- pitch) and development in ultra-dilute (ppm level TMAH) or even aqueous developers, presenting a greener and more precise resist platform for next-generation lithography.

A representative sequence-defined polypeptoid, composed of six t-butyl ester and four phenol repeating units with a terminal carboxylic acid (Fig.1) was synthesized via solid-phase submonomer synthesis, purified by high-performance liquid chromatography (HPLC), and confirmed to be molecularly homogeneous by liquid chromatography-mass spectrometry (LC-MS). Its low molecular weight combined with a single molecular species enables high-resolution lithography. It is fully compatible with standard lithographic processes, forming homogeneous films via spin coating. Upon EUV or e-beam exposure, terminal carboxylic acids undergo decarboxylation, leading to CO2 outgassing and increased hydrophobicity. Patterns are developed without a post-exposure bake using a highly diluted (ppm-level) TMAH solution, or in some other sequences, deionized water, enabling an eco-friendly process.

These resists exhibit negative-tone behavior under both e-beam and EUV, and achieve resolutions 14 nm half-pitch under EUV (Fig. 2), demonstrating high patterning fidelity under both exposure methods. The decarboxylation-based mechanism has been confirmed with mass spectrometry analysis on post- exposure films and outgassing experiments.



Chemical Formula: $C_{94}H_{136}N_{10}O_{27}$
Exact Mass: 1836.96
Molecular Weight: 1838.17

Figure 1: Molecular structure of the example polypeptoid sequence.

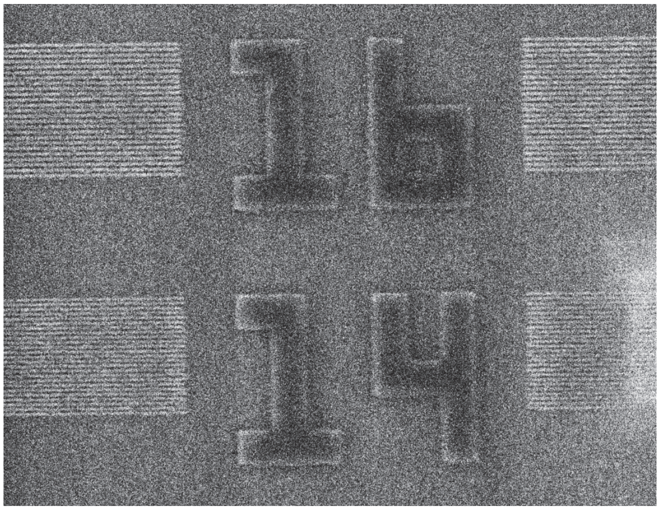


Figure 2: SEM image of EUV patterns showing 16- and 14-nm half-pitch line/space resolution.

Conclusions and Future Steps:

Our current research focuses on further improving patterning performance by screening libraries of selected polypeptoid sequences in which multiple carboxylic acid solubility-switch groups are positioned along the backbone, rather than one group exclusively at the chain end. We are also developing strategies to incorporate metal atoms with high EUV absorption into the polypeptoids to enhance sensitivity.

References:

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