Sequence-Defined Peptoids as Next-Generation EUV Photoresists

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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

Abstract:

Photoresists face substantial challenges as photolithography advances into the extreme ultraviolet (EUV) era. Traditional polymeric photoresists struggle with chemical randomness due to variations in polymer chains' molecular weight, composition, and sequence, as well as the unpredictable distribution and potential aggregation of photoacid generators (PAGs) within the polymer matrix. Additionally, the use of PAGs has sparked growing environmental concerns worldwide, especially since most commercially used PAGs are per- and polyfluorinated substances (PFAS). We have engineered sequence-defined polypeptoids to function as photoresists, addressing many existing limitations.

We developed a resist system that is a single-component monomolecular system composed solely of polypeptoids. The polypeptoids were synthesized by the solid-phase submonomer synthesis method [1]. The sequence typically includes phenol derivatives that induce solubility changes upon exposure to ionizing radiations including electronic beam (e-beam) or extreme UV (EUV), along with inactive building blocks, all precisely controlled at the molecular level. This design ensures uniform length, composition, and sequence, greatly minimizing compositional stochastics. The developed photoresist platform, incorporating phenol derivatives, is inherently patternable under EUV or e-beam lithography, removing the need for PAGs or other additives in the resist formulation. This innovation addresses problems related to uneven PAG distribution and tackles environmental, health, and regulatory concerns associated with PAGs in photoresist formulations. EUV patterning experiments demonstrated that the photoresist could achieve patterning at a 14 nm half-pitch or smaller resolution using an aqueous tetramethylammonium hydroxide solution as the developer.

Summary of Research:

We have developed a novel sequence-defined polypeptoid photoresist to address challenges in EUV lithography. Traditional polymeric photoresists struggle with compositional stochasticity originated from the random nature of conventional polymers in terms of molecular weight, composition and sequence, and there are also environmental concerns due to the use of PAGs with are mostly fluorinated compounds [2]. The new polypeptoid photoresist system, synthesized via solid-phase submonomer synthesis, features precisely positioned functional groups and exhibits uniform chain length, composition, and sequence. This can be proven by liquid chromatography–mass spectrometry (LC-MS) measurements (Figure 1). The wide variety of building blocks we can choose also allows us to explore new patterning mechanisms that have not been applied in advanced EUV photoresist design. This system mitigates stochastic effects and allows for intrinsic patternability under EUV radiation, eliminating the need for PAGs and thereby addressing related environmental concerns.

Our research involves extensive screening of peptoid sequences with various building blocks, such as tBOC-protected phenols, t-butyl esters, and unprotected phenols. Initial testing revealed that certain peptoid sequences demonstrated a negative tone pattern when developed in highly dilute aqueous base solutions, despite being designed to mimic the composition of conventional chemically amplified photoresists. This negative tone was first observed in peptoid sequences during development in a diluted tetramethylammonium hydroxide (TMAH) solution, and further confirmed using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

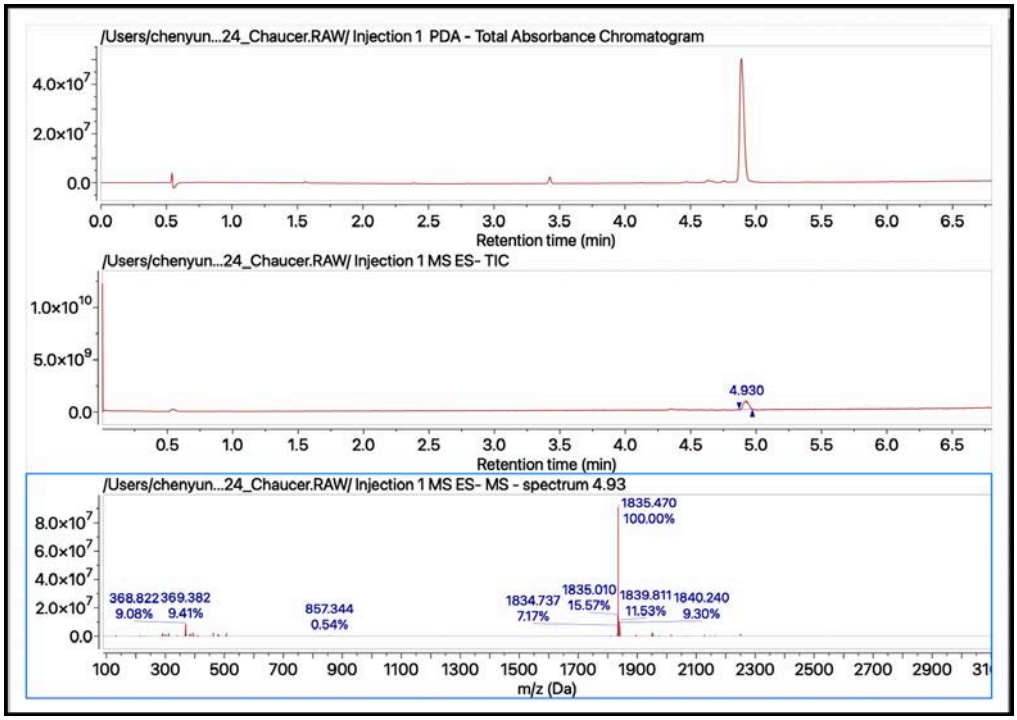

Figure 1: LC-MS data of one example polypeptoid sequence with theoretical molar mass 1836.96 g/mol.

Experiments indicated that these peptoids could be patterned in a negative tone under e-beam and EUV lithography, both with and without the presence of PAGs. However, the resolution improved significantly without PAGs, achieving a resolution of 24-nm half-pitch (hp) under e-beam lithography (Figure 2). Further testing at Lawrence Berkeley National Laboratory (LBNL) demonstrated that the peptoid sequences achieved a 14-nm hp resolution under EUV exposure without PAGs (Figure 3).

Our current efforts focus on understanding the underlying mechanisms and high-throughput synthesis of diverse peptoid sequences. The research confirmed that the negative tone mechanism is due to phenol groups in the structure, with chemistry occurring during exposure and potentially obviating the need for post-exposure baking (PEB). This phenol-based patterning mechanism has not been used in photoresist design previously, marking a significant advancement in photoresist technology.

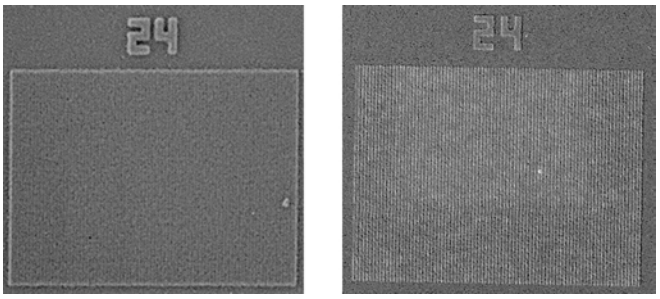

Figure 2: 24-nm half-pitch e-beam patterns of the polypeptoid resist. Left: with 10 wt% PAG. Right: without PAG. The no PAG sample required ~ 3 times dosage than the PAG containing sample.

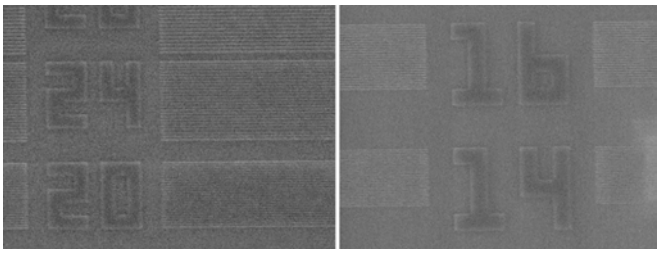

Figure 3: EUV patterns generated from the polypeptoid resist. Left: with 10 wt% PAG, 27 mJ/cm². Right: without PAG, 45 mJ/cm².

References:

[1] R. N. Zuckermann, J. M. Kerr, S. B. H. Kent, and W. H. Moos, "Efficient method for the preparation of peptoids [oligo(N-substituted glycines)] by submonomer solid-phase synthesis," J. Am. Chem. Soc., vol. 114, no. 26, pp. 10646-10647, 1992, doi: 10.1021/ja00052a076.

[2] C. K. Ober, F. Käfer, and C. Yuan, "Recent developments in photoresists for extreme-ultraviolet lithography," Polymer, vol. 280, 2023, doi: 10.1016/j.polymer.2023.126020.