Sequence-Defined Polypeptoid CARs for Electron-Beam and EUV Lithography

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Abstract:

Polymeric photoresists are limited in sensitivity, resolution, and line-edge roughness largely due to their various molar mass distributions and polymer chain compositions. Polypeptoids are, however, characterized by low stochastics. In this work we describe the synthesis of ten repeating-unit polypeptoids designed as photopolymers and demonstrate their potential as chemically amplified resists (CARs) evaluated by electron-beam (E-Beam), deep ultraviolet (DUV) and extreme-ultraviolet lithography (EUVL), obtaining well-defined line-space patterns of less than 30 nm half-pitch.

Summary of Research:

While in the last decade there has been significant progress on the design and synthesis of resists for EUVL, shortcomings of these resists still exist [1-3]. Despite the novel inorganic and metal-organic systems with good lithographic performance, their design is limited by their molecular structure [4]. For polymeric resist, their intrinsic defects always limit their lithographic performance [5]. In this work, we demonstrate the synthesis of polypeptoids whose structure, molecular weight, composition, and microstructure can be precisely controlled via a sequence-defined synthetic method [6-8] and investigate their potential as resists for EUVL.

Several libraries of polypeptoid with ten repeating units were synthesized. In particular we focus on four polypeptoids of which the sequences were altered, see Figure 1. After synthesis the polypeptoids were characterized by differential scanning calorimetry (DSC) to determine the glass transition temperature, and matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) was applied to confirm the polypeptoid structure, as previously reported [7]. Di-*tert*-butyl decarbonate (tBOC) was used to protect the hydroxy groups to introduce solubility-switch ability. By introducing short aliphatic and bulky sidechains, we were able to further tailor the solubility and contrast and obtained a resist which is developable in dilute aqueous base. Furthermore, polypeptoids with chain-end hydrophobic sidechains presented a better lithographic. This is attributed to microstructure and the increasing chain-mobility.

The lithographic performance of the synthesized polypeptoids was evaluated by E-Beam lithography. The best performing scanning electron microscope (SEM) micrographs represent the polypeptoid with a block-like structure where the short aliphatic and bulky aromatic sidechains are placed at the termini of the polypeptoid chain, see Figure 2.

Figure 3 shows the EUVL contrast curve taken from Paul-Scherrer Institute (PSI) in Switzerland, which presents a clearing dose at around 10 mJ/cm^2 indicating a positive tone, sensitive resist, while the change in sequence did not significantly affect the dosage to clear. It is worth noting that our first experiments indicated that a change of tone occurs by aging the resist solution. This might be attributed to the stability of the carbonate protecting group, which is reduced by terminal carboxylic acids of the polypeptoid chain. However, further studies are required to better understand the effect of the end-groups of the polypeptoids on solution stability and lithographic performance.

Conclusions and Future Work:

In this work we demonstrate the synthesis of short polypeptoids and show their potential as resists for EUVL. By introducing hydrophobic-aliphatic and aromatic bulky sidechains the solubility change could be tailored to obtain an aqueous-base developable resist. While the compositions of the synthesized polypeptoids were the same, the sequence was varied, affecting the lithographic performance. However, the best performance was observed placing the hydrophobic moieties closer to the chain ends, forming a symmetrical segmented structure, obtaining line: space patterns of 36 nm half-pitch by E-Beam lithography. The clear dosage of the best performing EUV resist was determined to be about 10 mJ/cm^2 showing a sharp change in solubility with increasing dosage. While we could successfully show the potential application of these materials as EUV resist, further research is required to optimize the lithographic performance, improve the stability in solution and identify the effect of sequence on lithographic patterning.

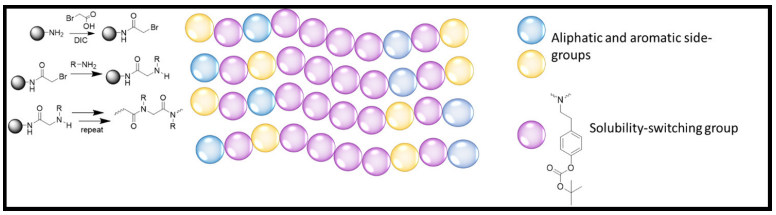

Figure 1: Solid phase supported synthesis of four different sequences of polypeptoid with short hydrophobic aliphatic and bulky aromatic side chains.

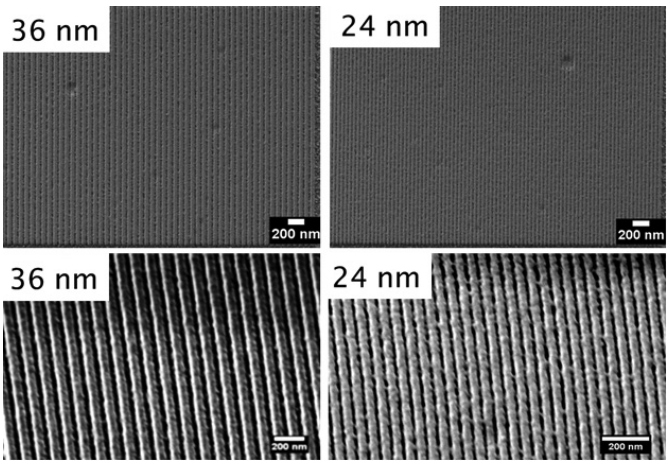

Figure 2: Electron-beam 1:1 line: space micrographs of the best performing polypeptoid developed in dilute 0.1 TMAH aqueous solution for 20s. PAG: TPS-PFBS (20 wt.%), Dosage: 216μC/cm^2.

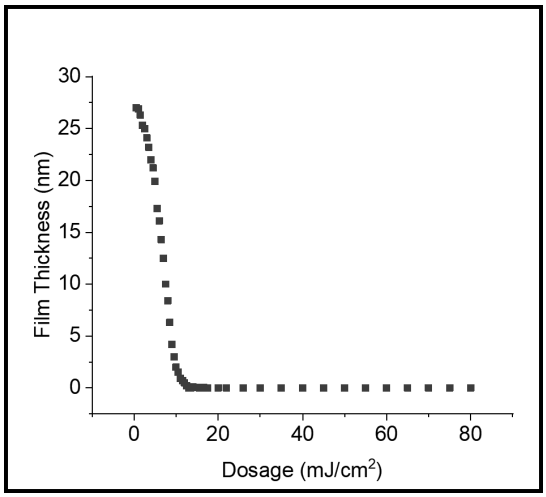

Figure 3: EUV contrast curve of a block-like polypeptoid with a short aliphatic and bulky aromatic sidechain at both termini.

References:

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