

PROCEEDINGS OF SPIE

SPIDigitalLibrary.org/conference-proceedings-of-spie

Sequence-defined polypeptoid CARs for electron-beam and EUV lithography

Florian Kaefer, Christopher Ober, Zoey Meng, Rachel Segalman, Javier Read de Alaniz

Florian Kaefer, Christopher K. Ober, Zoey Meng, Rachel Segalman, Javier Read de Alaniz, "Sequence-defined polypeptoid CARs for electron-beam and EUV lithography," Proc. SPIE 12498, Advances in Patterning Materials and Processes XL, 1249817 (30 April 2023); doi: 10.1117/12.2658413

SPIE.

Event: SPIE Advanced Lithography + Patterning, 2023, San Jose, California, United States

Sequence-defined polypeptoid CARs for electron-beam and EUV lithography

Florian Kaefer,^a Christopher K. Ober,^a Zoey Meng,^b Rachel Segalman,^b Javier Read de Alaniz^c

^aMaterials Science and Engineering, Cornell University, Ithaca, NY 14853; ^bMaterials Research Laboratory, UC Santa Barbara, Santa Barbara, CA, 93106; ^c Department of Chemistry & Biochemistry, UC Santa Barbara, Santa Barbara, CA 93106

ABSTRACT

Polymeric photoresists are limited in their sensitivity, resolution, and line-edge roughness due in large part to their molar mass distribution and variation in composition of single polymer chains. While most synthetic polymers, have monomer units distributed randomly along the polymer chain, polypeptoids are, however, characterized by low stochasticity i.e., identical chains with extremely low chemical, structural, and molar mass variability with a widely adjustable length and composition. In this work we describe the synthesis of 10 repeat-unit polypeptoids designed as a photopolymer and demonstrate their potential as CARs evaluated by electron-beam, DUV and extreme-UV lithography, obtaining well defined line-space patterns of less than 30 nm half-pitch.

Keywords: photoresists, polypeptoids, sequence-defined, extreme-ultraviolet lithography, electron-beam

INTRODUCTION

While in the last decade there has been significant progress on the design and synthesis of resists for extreme-ultraviolet lithography (EUVL) shortcomings of these resists still exist.[1-3] Even though the technical development of inorganic and metal-organic compounds with good lithography performance their design is limited by their molecular structure.[4] For polymeric resist on the other hand, lithographic performance can be widely tailored by changing polymer composition, architecture or molecular weight. However, the inhomogeneity/variations in molecular weight, composition, and miscibility issues of added compounds such as photoacid generator (PAG) is assumed to be a limiting factor in terms of their lithographic performance i.e., high line-edge roughness and low resolution.[5] In the past there have been studies addressing these shortcomings by developing new types of resists. Previously we demonstrated the potential of polypeptoids as a new type of photoresist [6, 7] whose structure, molecular weight, composition, and microstructure can be precisely controlled as all chains have the same molecular weight and composition. Furthermore, the incorporation of functionalities such as click-handles opens the possibility for polypeptoids used as a modular building block where properties such as adhesion, solubility contrast and thermal properties can be tailored quickly and over a wide range.

In this work we demonstrate the synthesis of polypeptoids and their potential as resists for EUVL. Polypeptoids were synthesized using a solid phase supported approach as previously reported.[8] While tBOC protected phenolic groups were used as a solubility switching group, short aliphatic and bulky aromatic side chains were used to tune the solubility towards an aqueous base developable resist resulting in an improved lithographic performance.

METHODOLOGY

Synthesis of Polypeptoids

All reagents and solvents were purchased from Sigma-Aldrich and used without further purification. Polypeptoids with ten repeat units were synthesized using a CSBio Peptide Synthesizer, Model CS336X. For the solid-phase supported synthesis of the polypeptoids 1g of 2-chlorotrityl chloride resin was swollen in with dimethyl-formamide (DMF). A first bromo acetylation step was carried out by adding 10 mL of a 1.3 M bromoacetic acid (BrAA) in DMF and 10 mL of a 1.3 M N, N-diisopropylethylamine (DIEA) in DMF to the resin and bubbling with nitrogen while shaking for 30 minutes. The resin was then washed repeatedly with DMF. Amination was performed by reacting the

acylated resin with 1-2 M of the amine in DMF for 60 minutes constantly bubbling nitrogen and shaking the reactor. Additional bromoacylation steps were conducted with 1.2 M BrAA and 1.4 M *N,N'*-diisopropylcarbodiimide (DIC) in DMF. Cleavage was accomplished by treatment with 20% hexafluoroisopropanol in dichloromethane (DCM). The resin was filtered, and the solution was concentrated via rotary evaporation and lyophilized. The resulting solid was dissolved in 1:1 acetonitrile/water and purified using a preparative HPLC and lyophilized and characterized using a Matrix Assisted Laser Desorption - Time of Flight (MALDI-TOF) Bruker AutoFlex Max tool. To introduce solubility switching groups the tyramine hydroxyl groups were protected with di-tert-butyl dicarbonate (tBOC). For the 1g peptoid synthesis, it was dissolved in 10 mL acetone and 1.3 equivalents of tBOC and 0.1 mol equivalent 4-dimethylaminopyridine (DMAP), were added and the solution was stirred for 24 hours at room temperature. Afterwards, the sample was concentrated, purified by preparative HPLC and lyophilized. The resulting solid was characterized using MALDI-TOF.

Lithographic evaluation

The polypeptoid resists were spin-coated from a propylene glycol methyl ether (PGME) solution with a concentration of 10mg/mL adding 20wt% photoacid generator - triphenyl sulfonium nonaflate (TPS-Nf). Pre-exposure and post-exposure bake were done at 80°C for 60s. For electron-beam exposures peptoid was dissolved in 1ml of propylene glycol methyl ether and 20 wt.% (in respect to peptoid) photoacid generator (TPS-nonaflate) was added and the solution was sonicated for 5min. The solution was filtered, and spin coated on a UVO cleaned silicon wafer. The coated wafer was post-apply baked for 60s at 90°C. E-beam exposures were performed using a JEOL 6300, 100kV e-beam tool. Extreme-ultraviolet exposures were conducted at the Paul-Scherrer Institute (PSI) in Switzerland. After exposure, the patterns were post-exposure baked for 60s at 110°C for 60s and developed in isopropyl alcohol. The resulting patterns were characterized using a Zeiss-Gemini-500-FESEM.

RESULTS AND DISCUSSION

Several libraries of polypeptoids with ten repeat-units were synthesized having the same composition using a solid-phase supported synthesis approach. In particular we focus on 4 polypeptoids in which the sequence was altered, see Figure 1. After synthesis the polypeptoids were characterized by DSC to determine the glass transition temperature, and MALDI-TOF was applied to confirm the polypeptoid structure, as previously reported.[7] For the change in solubility upon exposure, tyramine was used as an amine for the polypeptoid synthesis, and the phenolic hydroxyl group was tBOC protected after first cleaving the polypeptoids from their solid support and purifying them. In our previous work we have demonstrated that introduction of hydrophobic units such as propyne alters solubility as well as solubility contrast depending on the sequence of the polypeptoid while otherwise possessing the same chain composition. However, it was found that the hydrophilic amide backbone restricts potential developing conditions to organic developers such as isopropyl alcohol. Furthermore, it was found that introducing more hydrophobic sidechains results in better lithographic performance.

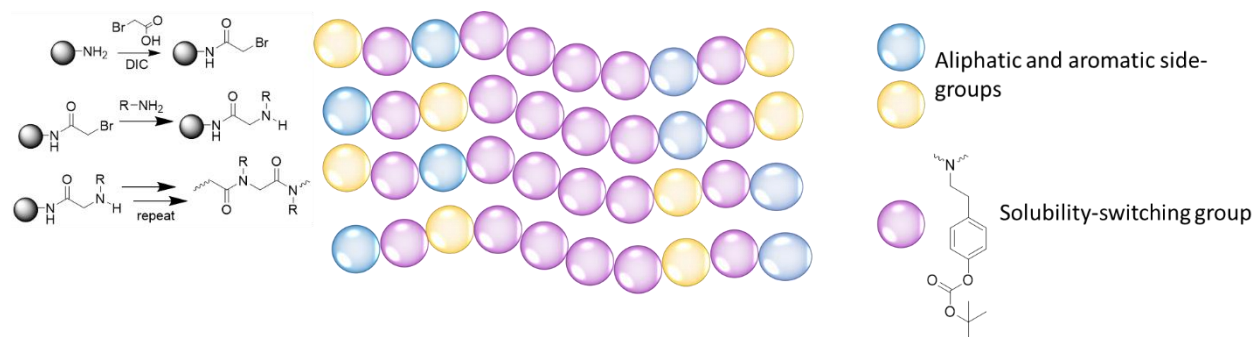


Figure 1. Solid phase supported synthesis of four different sequences of polypeptoid with short hydrophobic aliphatic and bulky aromatic side chains using tBOC protected phenolic hydroxyl groups to introduce a solubility switching group.

By introducing short aliphatic and bulky sidechains in this work we were able to further tailor the solubility and contrast and obtained a resist which is developable in dilute aqueous base. Furthermore, it was found that consistent with our previous findings the sequence controls the dissolution behavior and lithographic performance.[8] Placing the hydrophobic sidechains at the chain-ends of the polypeptoid resulted in a better lithographic performance i.e., a higher resolution using EBL. This is assumed to be due to microstructure and the increasing chain-mobility.

The lithographic performance of the synthesized polypeptoids was evaluated by e-beam lithography. Representative images show the e-beam 1:1 line space pattern SEM micrographs obtained for the best performing 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. Defined 1:1 line space patterns of 36 nm half-pitch were obtained while 24 nm half-pitch pattern exhibit height roughness, bridging and other defects.

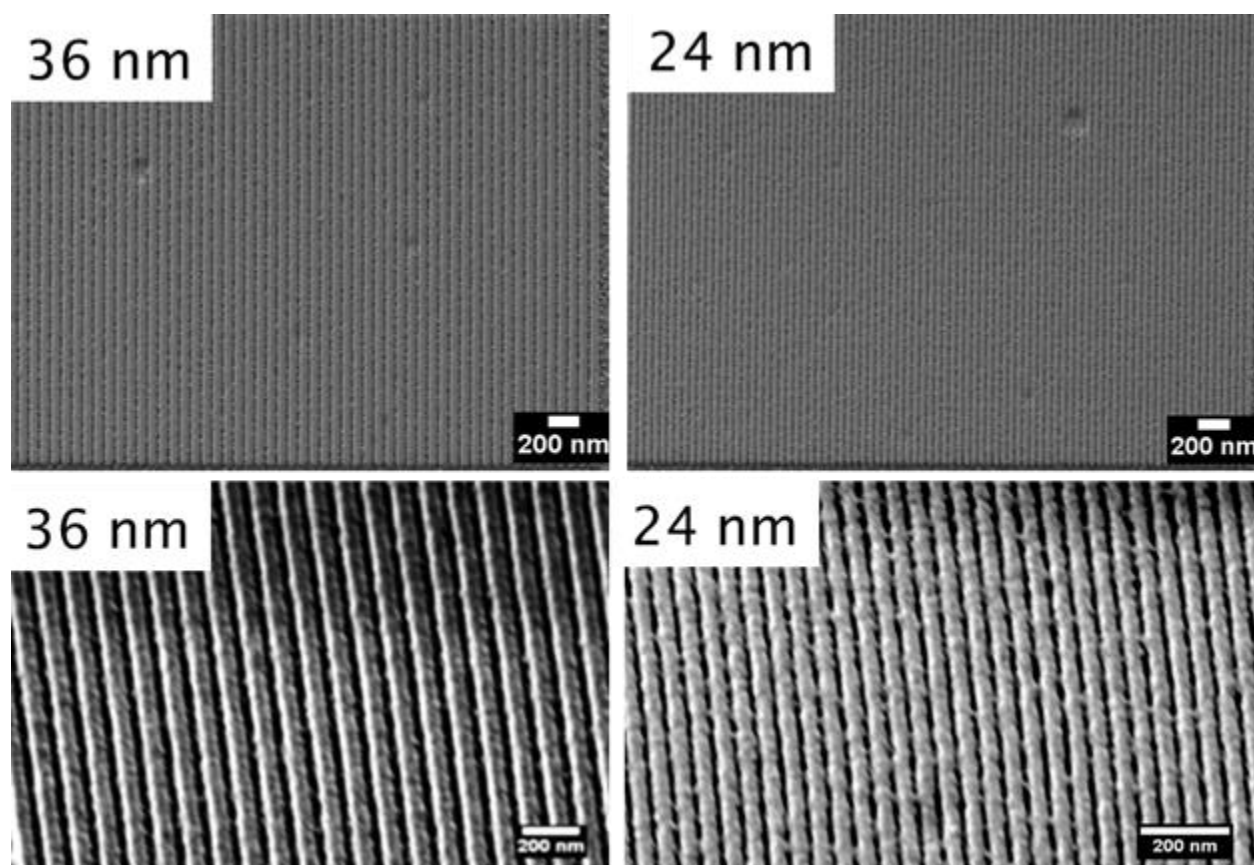


Figure 2. Electron-beam 1:1 line: space micrographs of the best performing polypeptoid developed in dilute 0.1 TMAH aqueous solution for 20s. PAG: TPS-PFBS (20 wt.%), Dosage: $216\mu\text{C}/\text{cm}^2$.

Based on the lithographic performance determined by electron-beam lithography, first EUVL contrast curves of the resists were determined at the Paul-Scherrer Institute, Switzerland, see Figure 3. The resulting contrast curves show a clearing dose at around $10\text{ mJ}/\text{cm}^2$ indicating a positive tone, sensitive resist, while the change in sequence did not significantly affect the dosage to clear. It is worth noting, 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.

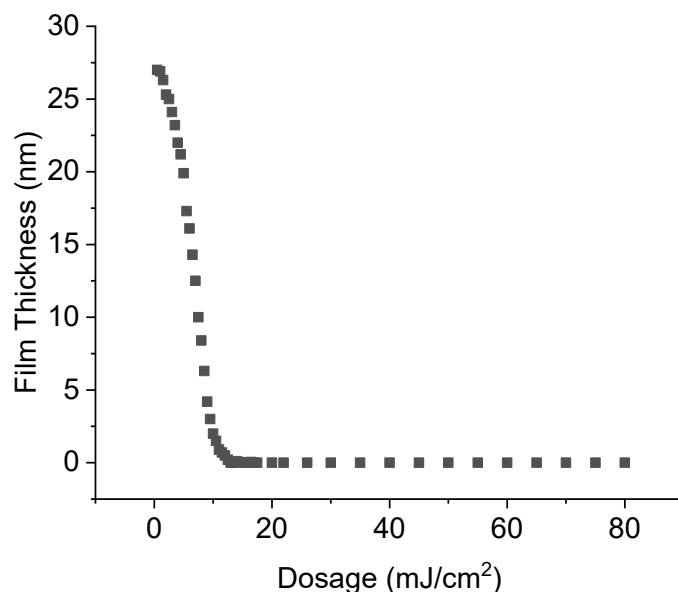


Figure 3. EUV contrast curve of a block-like polypeptoid with a short aliphatic and bulky aromatic side-chains at both termini.

CONCLUSIONS

In this work we demonstrate the synthesis of short (10 repeat units) polypeptoids and show their potential as resists for EUVL. By introducing hydrophobic-aliphatic and aromatic bulky side-chains 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, showed, and effected 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 36nm half-pitch by EBL. Preliminary EUV exposures were performed at the Paul-Scherrer Institute, Switzerland. The clear dosage of the best performing resist was determined to be about 10 mJ/cm² 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.

ACKNOWLEDGEMENTS

The authors thank the Intel Corporation for financial support of the CINEMA program. We would also like to thank the Paul-Scherrer Institute, Switzerland especially Michaela Vockenhuber for the EUVL experiments. This work was performed in part at the Cornell NanoScale Facility, an NNCI member supported by NSF Grant NNCI-2025233. Furthermore, this work made use of the Cornell Center for Materials Research Shared Facilities which are supported through the NSF MRSEC program (DMR-1719875).

REFERENCES

- [1] Lio, A., "EUV Photoresists: A Progress Report and Future Prospects," *Synchrotron Radiation News*, **32**(4): p. 9-14 (2019).
- [2] Li, L., et al., "Extreme ultraviolet resist materials for sub-7 nm patterning," *Chemical Society Reviews*, **46**(16): p. 4855-4866, (2017).
- [3] Manouras, T. and P. Argitis, "High Sensitivity Resists for EUV Lithography: A Review of Material Design Strategies and Performance Results," *Nanomaterials (Basel)*, **10**(8) (2020).
- [4] [4] Luo, C., et al., "Review of recent advances in inorganic photoresists," *RSC Advances*, **10**(14): p. 8385-8395, (2020).
- [5] Anna, L. "EUV resists: What's next?," in *Proc.SPIE*, (2016).
- [6] Deng, J., et al., "New Approaches to EUV Photoresists: Studies of Polyacetals and Polypeptoids to Expand the Photopolymer Toolbox," *Journal of Photopolymer Science and Technology*, **34**(1): p. 71-74, (2021).
- [7] Meng, X.Z., et al. "Controlled sequence peptoids as photoresist platforms for high-resolution DUV/EUV photoresists," *Proc.SPIE*, (2022).
- [8] Florian Kaefer, Z.M., Rachel Segalman, Christopher Ober. "Controlled Sequence Photoresists from Polypeptoids," *The 39th International Conference of Photopolymer Science and Technology*, (2022)