Peptoids as Sequence-Controlled EUV-Photoresists

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Primary CNF Tools Used: ABM contact aligner, ASML 300C DUV stepper, AFM Bruker Icon, FilMetrics F50-EXR

Abstract:

Sequence-controlled small molecules were synthesized using a peptide synthesizer. The thus obtained peptoids with an average molar mass of 1000 g/mol and a strong alternating sequence of the two used amines were used as positive tone resists for deep ultraviolet (DUV) and extreme ultraviolet (EUV) lithography. In our first experiments we could demonstrate the potential of peptoids as a promising class of new EUV resist, as both the structure of the used amines and the sequence can be adapted to precisely adjust the properties of the photoresist.

Summary of Research:

Introduction. Today's widely used polymeric resists are typically based on random copolymers. These polymers are polydisperse and relatively large in size, with molar masses ranging from 5,000-15,000 g/mol [1]. Characteristics such as these can have a negative impact on resist performance, and therefore it is necessary to explore other architectures for new resist platforms.

Sequence-Controlled Small Molecules. For sequence-controlled polymers, on the other hand, the monomers are arranged in a specific, user-defined order. Monomer sequence regularity strongly influences the molecular, supramolecular, and macroscopic properties of polymer materials, showing promise for the creation of a new type of small molecule photoresist. In this respect, peptoids represent a particularly advantageous group, since they can be specifically varied in their structure, length and sequence of the amines used [2].

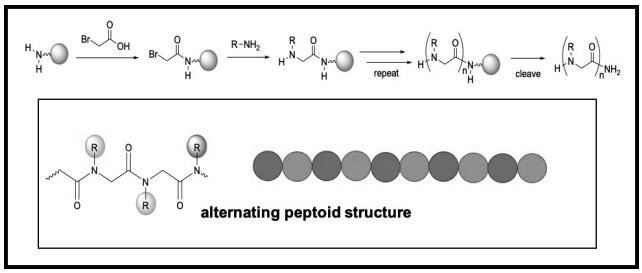

Figure 1: Synthesis of peptoids with an alternating amine sequence.

Peptoid Synthesis. A solid phase peptoid synthesis approach using a 2-chlorotrityl based resin was used [3]. After activating the resin with bromoacetic acid, the first amine solution was added. After the reaction was completed, the second amine, which contains a tert-butyl protecting group, was added and clicked to the resin. These steps were repeated until a peptoid with a total length of ten amines in alternating sequence was obtained, see Figure 1. Subsequently, the peptoid was cleaved from the resin under mild acetic conditions, purified and dried. In order to determine the molar mass and the molecular structure liquid chromatography-mass spectrometry was used.

Characterization and Results:

Preliminary photolithography experiments were performed on the ABM contact aligner and the DUV stepper. For this purpose, the produced peptoid sample with a molar mass of 1000 g/mol and an alternating amine sequence was dissolved, and spin-coated on a silica wafer.

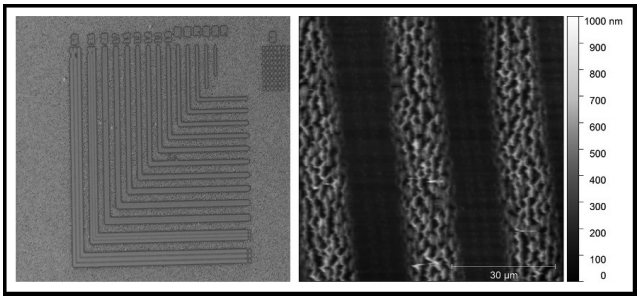

Figure 2: Patterned peptoid film after DUV exposure at the ABM contact aligner. (left) light microscopy image, (right) AFM image.

The resist film thickness was measured by FilMetrics F50-EXR. The made samples were exposed using the ABM contact aligner and developed using a diluted tetramethylammonium hydroxide (TMAH) solution. The obtained pattern was characterized using light microscopy and atomic force microscopy (AFM Bruker Icon), see Figure 2.

The measurements carried out successfully prove that peptoids can be used as DUV photoresist materials. However, the obtained results also show that further optimization of the peptoid structure as well as the photolitographic process requires further optimization. Especially the achieved resolution and the obtained mean roughness of 45 nm have to be improved.

Conclusions and Future Steps:

Sequence controlled peptoids with a molar mass of 1000 g/mol and with strong alternating sequence of the used amines could be synthesized and successfully used as positive tone photoresist using the ABM contact aligner. The obtained patterned films were characterized using light- and atomic force microscopy. However, several challenges still need to be solved. How do we design small molecules to make a photoresist with a desired property? How do we control the nanoscale resolution of the resulting resist? The aforementioned questions shall be studied and answered in the future.

References:

[1] Patterson, K.; Yamachika, M.; Hung, R.; Brodsky, C.; Yamada, S.; Somervell, M.; Osborn, B.; Hall, D.; Dukovic, G.; Byers, J.; Conley, W.; Willson, C. G., Polymers for 157-nm photoresist applications: a progress report. SPIE: 2000; Vol. 3999.

[2] Gangloff, N.; Ulbricht, J.; Lorson, T.; Schlaad, H.; Luxenhofer, R., Peptoids and Polypeptoids at the Frontier of Supra- and Macromolecular Engineering. Chemical Reviews 2016, 116 (4), 1753-1802.

[3] Culf, A. S.; Ouellette, R. J., Solid-phase synthesis of N-substituted glycine oligomers (alpha-peptoids) and derivatives. Molecules (Basel, Switzerland) 2010, 15 (8), 5282-5335.