A New Generation of Small Molecules for EUV Photolithography

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Primary CNF Tools Used: ASML 300C DUV stepper, JEOL 6300 electron-beam, Zeiss Ultra SEM, RC2 Woollam ellipsometer

Abstract:

Modern computer chips require smaller and smaller feature sizes in the 3 to 5 nm range to reach greater efficiencies. One way to achieve this is by using polymeric resists with well-defined repeat group sequences. In this research, peptoids, made of amine monomers, have been synthesized to contain identical sequences and very small chain sizes in a specific sample, allowing for higher pattern resolution. Azide-alkyne click chemistry has been used on the peptoid backbone to homogeneously introduce new functionalities to the peptoid. Peptoids of two different sequences were synthesized, and the photolithographic properties were investigated through deep ultraviolet (DUV) and electron-beam photolithography exposures.

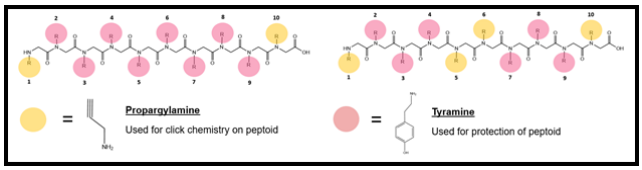

Figure 1: Chosen sequences for peptoid samples, 181-ProT on left and 13231-ProT on right.

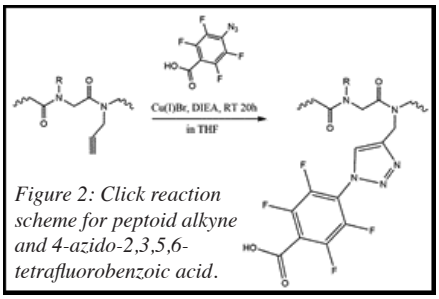

Figure 2: Click reaction scheme for peptoid alkyne and 4-azido-2,3,5,6-tetrafluorobenzoic acid.

Summary of Research:

In this work, we utilize click chemistry on a small, sequence-controllable molecule, called a peptoid, to generate a new polymeric photoresist material. Click chemistry is a category of highly specific, high yield, fast reactions that form a bond between two particular chemical handles [1].

Two peptoids were synthesized to contain 10 units of different compositions of propargylamine (Pro) and tyramine (Tyr). The sequences were 181-ProT and 13231-ProT (Figure 1). The alkyne group of propargylamine served as a click handle, whereas tyramine was protected for photolithography exposures. The peptoid synthesis was performed using repeated acylation and replacement steps on 2-chlorotrityl chloride resin. The peptoid was cleaved from the resin and protected using di-tert-butyl dicarbonate.

For the click reaction, 1 equiv. of protected peptoid was stirred with 40 equiv. N,N-diisopropylethylamine, 2 equiv. Cu(I)Br, and 5 equiv. of 4-azido-2,3,5,6-tetrafluorobenzoic acid (Azo4FBA) in tetrahydrofuran (THF) for 20 hr at room temperature [2] (Figure 2). The fluorinated azido-acid was chosen for the purpose of increasing hydrophobicity of the resist and providing the first step for a homogeneously distributed photoacid generator.

The peptoid samples were characterized by differential scanning calorimetry (DSC), matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF), and nuclear magnetic resonance (NMR) spectroscopy. With DSC, the glass transition temperature of 181-ProT was determined to be 120°C. Through MALDI-TOF, the

theoretical mass of 181-ProT (2425.14 g/mol) was found, verifying the synthesis of the correct peptoid product. 1H-NMR of 181-ProT and 181-ProT-Clicked showed the disappearance of an alkyne-indicative proton peak around 3.03 ppm, while 19F-NMR data for 181-ProT-Clicked displayed a peak around -75 ppm, proving the successful clicking of Azo4FBA. The resist performance was determined through DUV and electron beam photolithography. Isopropanol was found to be the most effective developer for both sets of samples, 181-ProT and 13231-ProT, at a developing time of one minute. The RC2 Woollam ellipsometer was utilized to measure the film thickness of each box on the 181-ProT flat exposure to determine the best dose for DUV photolithography. Scanning electron microscopy (SEM) images were taken of the DUV line-space pattern and electron beam samples for further characterization.

This work found that adjusting the sequence of propargylamine and tyramine monomers changes the solubility and performance of the resist. Clear DUV and electron beam line-space patterns were observed (Figures 3 and 4), signifying good resolution. Additionally, the successful peptoid azide-alkyne cycloaddition indicates that click reactions allow easy modification of peptoid resist properties. In the future, new azides with different functionalities will be clicked on Pro-Tyr peptoids to alter resist properties such as solubility, glass transition temperature, and resist performance. Altogether, this research has explored a promising avenue for polymeric photoresist development for EUV photolithography.

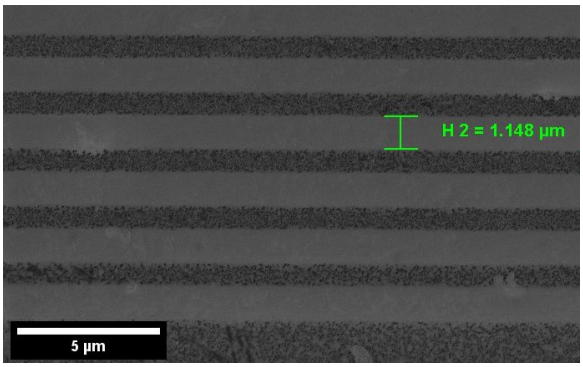

Figure 3: SEM image of 1.15 µm line pattern from DUV exposure on 181-ProT.

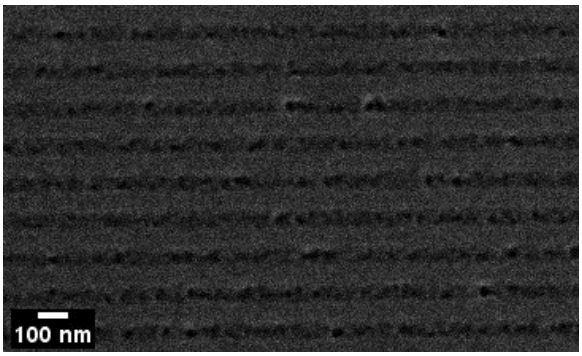

Figure 4: SEM image of 83 nm line pattern from e-beam exposure on 13231-ProT.

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References:

[1] Castro, V.; Rodríguez, H.; and Albericio, F. CuAAC: An Efficient Click Chemistry Reaction on Solid Phase. ACS Comb. Sci. 2016 18 (1), 1-14.

[2] Thundimadathil, J. Click Chemistry in Peptide Science: a Mini-Review. Chimica Oggi -Chemistry Today. 2013 31 (2), 34-37.