New Generation of DUV Photoresists with Precise Molecular Structure

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

Abstract:

This CNF internship project is focused on synthesizing peptoids, with a controlled sequence of amines and chain length, to be used as photoresist materials. As photoresist materials, these peptoids must be UV sensitive, changing solubility when exposed to UV light. 10-mers (peptoids with 10 repeat units) are created with different compositions and sequences of amines to optimize the pattern resolution of the photoresist. These positive tone chemically amplified photoresists are exposed with deep ultraviolet (DUV) to create line patterns ranging from 1-0.1 μm. The line patterns are analyzed to determine the effect of the chosen composition and sequence.

Summary of Research:

Introduction. Photoresists are typically made of polymers that are polydisperse and whose monomers are randomly distributed along the chain. These attributes bottleneck the ability to attain smaller feature sizes since the dispersity and length affects photoresist properties. Therefore, it is imperative to create new materials where the sequence and chain length can be controlled, like peptoids.

Peptoid Synthesis and Characterization. The peptoids are synthesized by adding each amine to 2-chlorotrityl chloride resin. The resin is activated through bromoacetylation, and then the amine is added by displacing the bromine (see Figure 1).

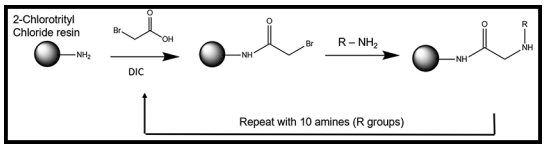

Figure 1: Peptoid synthesis on 2-chlorotrityl chloride resin through bromoacetylation and displacement until all ten amines (R groups) are added.

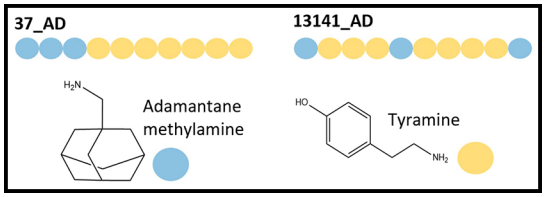

Figure 2: Peptoid amine sequence of samples 37_AD and 13141_AD.

This process repeats until all 10 amines are added to the chain. The samples have different sequences but the same composition — 3 adamantane methylamine (AD) and 7 tyramine (TA). Sample 37_AD has sequence $AD_{(3)}$–$TA_{(7)}$, and sample 13141_AD has sequence $AD_{(1)}$–$TA_{(3)}$–$AD_{(1)}$–$TA_{(4)}$–$AD_{(1)}$ (see Figure 2).

Afterward, the peptoids are cleaved off the resin using mild acid, protected, and purified. The amine, tyramine, present in all samples, is protected using di-*tert*-butyl dicarbonate. Exposure to UV light deprotects tyramine, changing its chemical structure and solubility. The samples are then purified using preparative high-performance liquid chromatography (HPLC). The glass transition temperature of the peptoids is determined through differential scanning calorimetry (DSC), and the mass is verified through liquid chromatography-mass spectrometry (LC-MS).

Exposures. For spin coating, the peptoids are dissolved in organic solvent and a photoacid generator is added. The solution is then sonicated and filtered to degas before spin coating on a silica wafer. The wafer is baked (pre and post) at the glass transition temperature of the peptoids. The wafer is then exposed using the ASML 300C DUV stepper to print line and resolution patterns.

Solubility and SEM Images. Following exposures, the film is tested for different developers at various times to remove the exposed/unprotected regions on the film. To optimize contrast, there must be a great difference in solubility before (protected) and after exposures (unprotected). The

solubility before and after exposures differ between the two samples (see Figure 3). After developing the film, the patterns are observed and analyzed using scanning electron microscopy (SEM). As shown in Figure 4, these peptoids produce clear patterns smaller than 0.4 μm, which is already approaching the limits of DUV lithography (0.2 μm). After being developed in ethyl acetate for 45 seconds, 13141_AD produced clear line patterns of 0.4 μm. Sample 37_AD was developed in ethyl acetate for two minutes and produced clear line patterns of 0.3 μm.

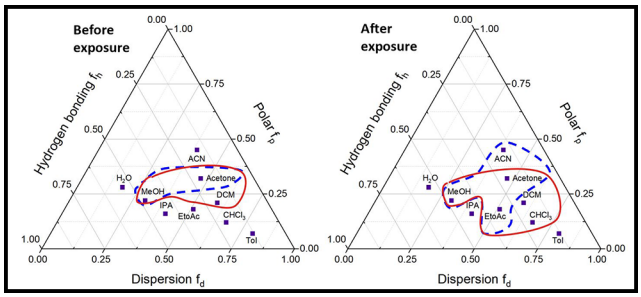

Figure 3: TEAS plots showing the solubility for samples 37_AD (blue dotted lines) and 13141_AD (red solid lines) before and after exposures.

Conclusions and Future Steps:

Although these samples have the same composition, their solubility is different before and after exposures. This suggests that the sequence of amines influences solubility and contrast, and is thus an important factor when optimizing the photolithography performance. Patterns this small (0.4 and 0.3 μm) and clear are promising results for even smaller feature sizes that are possible to print with e-beam and extreme ultraviolet (EUV) exposures. We will perform e-beam exposures with the JEOL 6500 and EUV exposures with Intel. Furthermore, to have greater control over the placement of the photoacid generators, we will be including a photoacid generator as one of the amines of the 10-mer. This will guarantee a more homogenous film and distribution of the photoacid generator.

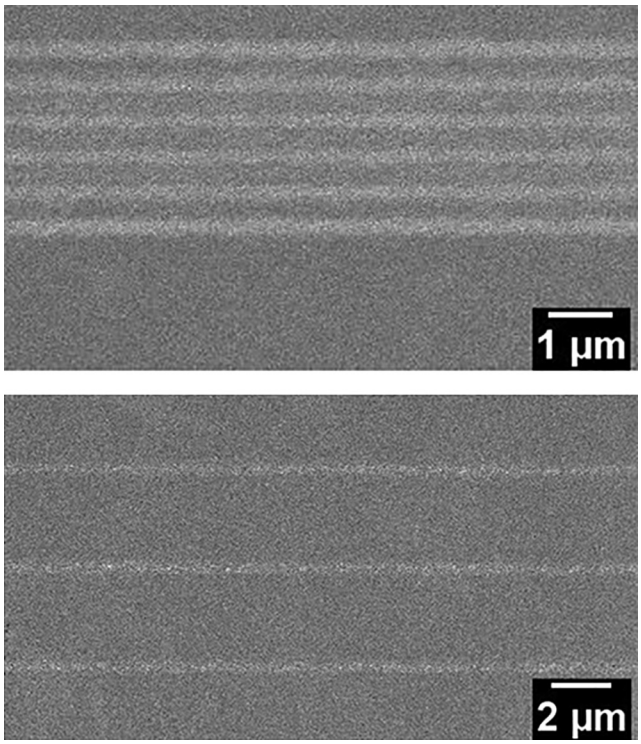

Figure 4: SEM images of line space patterns of (top) 37_AD and (bottom) 13141_AD; developed in ethyl acetate for two minutes and 45 seconds, respectively.

Acknowledgments:

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