Scissionable Polymer Photoresist for Extreme Ultraviolet Lithography

CNF Project Number: 2751-18
Principal Investigator(s): Christopher Kemper Ober
User(s): Jingyuan Deng

Affiliation(s): Materials Science and Engineering, Cornell University

Primary Source(s) of Research Funding: INTEL Corporation

Contact: c.ober@cornell.edu, jd966@cornell.edu

Primary CNF Tools Used: ASML 300C DUV Stepper,
JEOL 6300 E-Beam Lithography, P10 Profilometer

Abstract:

Scissionable polymers are polymers that will depolymerize under different stimuli including acid, base, and free radicals. These polymers have been investigated in the development of photoresists and other degradable materials. This work focuses on the poly(phthalaldehyde), PPA, a family of scissionable polymers. The PPA backbone consists of acetal linkages that are very sensitive to acids. Upon exposure to acids, the polymer chain depolymerizes to its corresponding monomers. This depolymerization behavior makes PPAs excellent candidates as photoresist materials. Several new PPA photoresists are being explored in this work.

Summary of Research:

Poly(phthalaldehyde) (PPA) is a well-established depolymerizable photoresist developed by IBM in 1983 [1]. Monomer outgassing and absence of bench-stability resulted in the resist being abandoned in favor deprotection based resists. However, multiple groups have recently explored the potential of PPA under EUV exposure [2-4], but so far success has been elusive. In comparison with other depolymerizable systems, a very limited number possess the same depolymerization kinetics, and those that do suffer from poor sensitivity or outgassing.

The difficulty in simultaneously maximizing resolution, line edge roughness, and sensitivity is known as the RLS trade-off and is one of the foremost issues hampering EUV performance. One accepted technique to bypass the RLS trade-off is to employ high loadings of photoacid generator (PAG) and in the process diminish deleterious shot noise effects. Unfortunately, the popular ionic PAGs phase separate regularly at elevated concentrations, especially above 20 wt%. Non-ionic PAGs present a potential solution to this problem as they can remain miscible at significantly higher concentrations compared to ionic PAGs. These PAGs also possess advantages in dark loss and acid yield when exposed to e-beam.

Despite the potential of non-ionic PAGs, they are consistently inferior to ionic PAGs in terms of sensitivity, with few able to achieve the requisite EUV dose-to-clear under 20 mJ/cm^2. This challenge has been worsened by the dearth of mechanistic information available concerning the behavior of non-ionic PAGs under EUV exposure.

In this report, we describe the development and photolithographic performance of photoresists consisting of a PPA derivative and a non-ionic PAG. We found that many simultaneously possessed high stability and remarkable EUV sensitivity.

Results and Discussions:

Photoresist polymers (35 mg) and photoacid generators (7 mg) were dissolved in 1 mL propylene glycol methyl ether acetate (PGMEA). The resist was spin-coated onto a silicon wafer at 3000 rpm for 1 min. The coated silicon wafers were then exposed using ASML 300C DUV stepper. After exposure, the exposed film was baked and developed. The resulting line-space patterns were characterized using AFM shown in Figure 1.

As seen from these figures, the relatively rough line edge roughness was caused by the acid diffusion, which could be alleviated by changing the chemical structure of the photoacid generator.

We further investigated these resist materials under EUV exposure. By using these non-ionic PAGs, we were able to achieve dose to clear for as low as 12 mJ/cm^2.

Summary:

In summary, preliminary results were obtained with chain scissionable photoresists. With these results in hand, the lithographic performance of newly developed functionalized PPAs will be investigated.

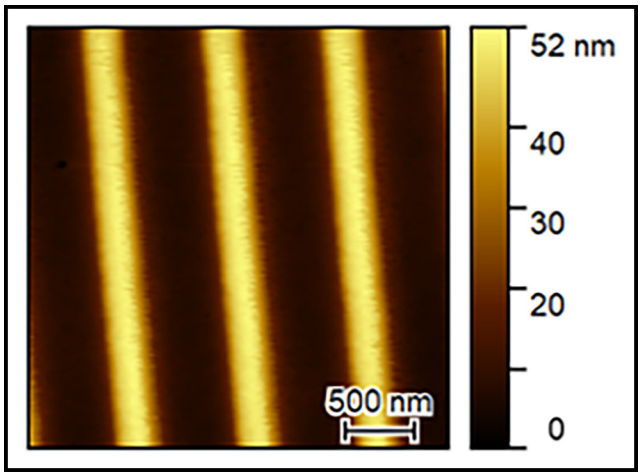

Figure 1: Line-space patterns characterized using AFM.

References:

[1] H. Ito, C. G. Willson, Polym. Eng. Sci., Chemical amplification in the design of dry developing resist materials, 1983, 23, 1012-1018.

[2] A. Rathore, I. Pollentier, S. S. Kumar, D. De Simone, S. De Gendt, J. Micro/Nanopattern. Mats. Metro., Feasibility of unzipping polymer polyphthalaldehyde for extreme ultraviolet lithography, 2021, 20, 034602.

[3] P. A. Kohl, A. Engler, C. Tobin, C. K. Lo, Journal of Materials Research, Influence of material and process parameters in the dry-development of positive-tone, polyaldehyde photoresist, 2020, 35, 2917-2924.

[4] J. Deng, F. Kaefer, S. Bailey, Y. Otsubo, Z. Meng, R. Segalman, C. K. Ober, J. Photopol. Sci. Technol., New Approaches to EUV Photoresists: Studies of Polyacetals and Polypeptoids to Expand the Photopolymer, 2021, 34, 71-74.