New High-Resolution Resists for EUV Lithography

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

Abstract:

The semiconductor industry depends on photoresists to manufacture advanced chips. To meet the industry's growing demands for precise pattern fidelity and resolution, scissionable polymeric materials with chain end groups that can trigger depolymerization are crucial. A promising solution is photodegradable polymer material based on poly(phthalaldehyde) (PPA), having acetal linkages highly sensitive to acids. When exposed to deep ultraviolet (DUV) or electron beam light, these end groups generate acids that induce depolymerization of PPA into its monomers. In this report, we describe the design and synthesis of bromo-substituted PPA and demonstrate its effectiveness as a photoresist through DUV lithography, achieving well-defined line-space patterns.

Summary of Research:

In 1983, IBM's research laboratory developed depolymerizable photoresists, including end-capped poly(phthalaldehyde) (PPA). These photoresists contain photolabile groups that generate acids when exposed to light. The acids then catalyse the chain cleavage of the PPA [1]. In the literature, various research groups have investigated the potential of PPA under DUV and EUV radiation. The Ober research group has demonstrated that functionalized poly(phthalaldehyde)s (PPAs) can serve as degradable polymer backbones. Additionally, this group has explored PAG-tethered phthalaldehyde to achieve exceptional results across several lithography techniques [2-4].

In this report, we have described the development of photoresists containing active end groups, which show high stability, low outgassing and extreme sensitivity under DUV exposure. The development and depolymerization mechanism of functionalized linear Br-PPA is shown in Figure 1. After exposure of EUV radiation, the EUV active end group initiates depolymerization via a cascade mechanism.

Result and Discussion:

The synthesized Br-PPA polymer was examined with 1H NMR spectroscopy to determine its structural confirmation and evaluate its stability, while its thermal stability was evaluated through thermogravimetric analysis. The molecular weight of the polymer was characterized via gel permeation chromatography.

For photoresist testing, 35 mg of the polymer was dissolved in 1 mL of cyclohexanone and spin-coated onto a silicon wafer at 2500 rpm for 60 seconds. The coated wafers were then subjected to DUV radiation using an ASML 300C DUV stepper. After radiation exposure, the film was baked at 90°C and developed in isopropyl alcohol for 30 seconds. The resulting line-space patterns were examined using Atomic Force Microscopy (AFM), as depicted in Figure 2.

Conclusions and Future Work:

In this work, we demonstrate the synthesis of bromo-substituted poly(phthalaldehyde) (Br-PPA) with active end groups and observed its potential as a photoresist for deep ultraviolet (DUV) lithography. The initial results with the Br-PPA are promising. Moving forward, we will further explore the lithographic performance of various functionalized PPA photoresists.

References:

[1] Ito, H.; Willson, C. G. Chemical Amplification in the Design of Dry Developing Resist Materials, Polym. Eng. Sci. 23, 1983, 1012-1018.

[2] Deng, J., Bailey, S., Jiang, S., Ober, C. K. High-Performance Chain Scissionable Resists for Extreme Ultraviolet Lithography: Discovery of the Photoacid Generator Structure and Mechanism. Chem. Mater. 2022, 34, 6170.6181.

[3] Deng, J., Bailey, S., Ai, R., Delmonico, A., Denbeaux, G., Jiang, S., Ober, C. K. Synthesis of End-Cap Enabled Self-Immolative Photoresists For Extreme Ultraviolet Lithography. Macro Lett. 2022, 11, 1049.1054.

[4] Deng, J., Bailey, S., Jiang, S., Ober, C. K. Modular Synthesis of Phthalaldehyde Derivatives Enabling Access to Photoacid Generator-Bound Self-Immolative Polymer Resists with Next-Generation Photolithographic Properties. J. Am. Chem. Soc. 2022, 144, 42, 19508-19520.

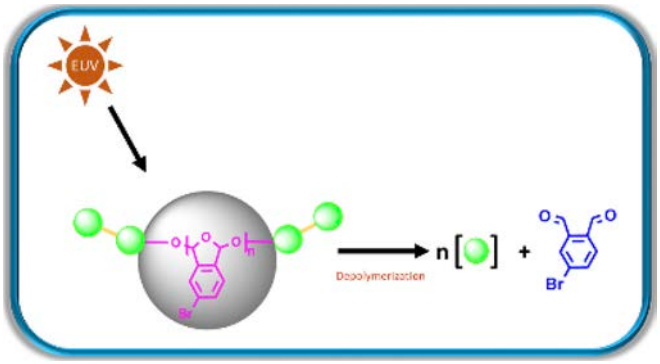

Figure 1: Functionalized linear Br-PPA with photoactive end groups.

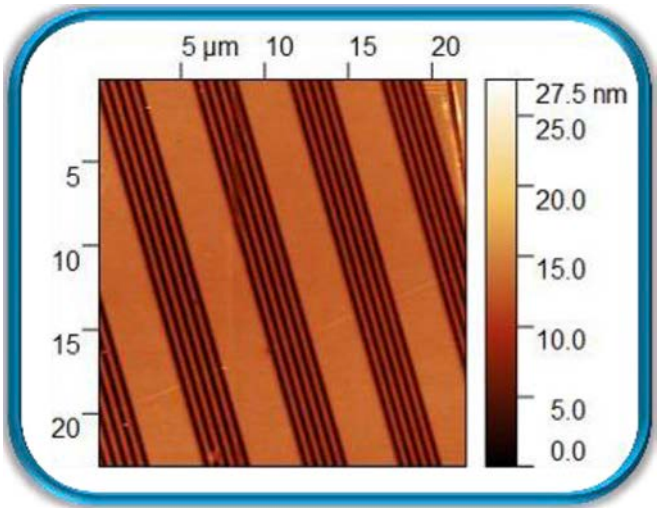

Figure 2: Line-space patterns characterized using AFM.