Analysis of EUV Induced Depolymerization of Polyphthalaldehydes and Side Reactions for Dry Develop EUV Resist Applications

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Supplementary Information

1. Contrast Curve with Wet and Dry Development



Figure S1 – Thickness contrast curve of PA-25 after EUV exposure. A comparison of no development and wet development with IPA is shown. The reduction in thickness between two development methods is minimal. The film thickness is not removed fully by IPA, indicating presence of larger molecules.

2. Nuclear Magnetic Resonance (NMR)

Samples for NMR spectra were prepared by coating 50 nm thick PA-25 on a 200 mm Si wafer. A large area of the wafer was exposed to EUV radiation with a dose of 6.5 mJ/cm². The wafer was cleaved to separate exposed from unexposed regions. The exposed portions were washed with deuterated dimethyl sulfoxide (DMSO-d6) for nuclear magnetic resonance (NMR) analysis. The spectra were collected on a Bruker Avance III 400 MHz instrument in the Georgia Tech NMR facility. Chemical shifts are reported in δ (ppm) relative to the tetramethyl silane internal standard ($\delta = 0$ ppm).

Figure S2 and S3 show ¹H-NMR spectra of un-exposed and exposed regions of PA-25 respectively. The region around 7.25 ppm is of particular importance for the analysis of phthalaldehyde-based resists and potential aromatic byproducts. This chemical shift region represents protons on the backbone of the polymer (peaks b, c) as well as protons attached to aromatic ring of an ester (Figure S3, peaks p, q), which could form after radical formation of phthalaldehyde. These ester peaks are particularly high in the exposed sample as confirmed by integration although reliable integration of them is difficult due to the low signal-to-noise ratio. The presence of a stronger relative signal in the exposed sample points to the formation of an aromatic ester. The chemical shift of the aromatic aldehyde (peak s) does not correspond to phthalaldehyde monomer, which leads us to believe the formation of another byproduct species that cannot be identified solely through NMR due to peak convolution with the remaining polymer peaks. Gaining insight from the NMR and reaction scheme illustrated in reference¹ for the excited state of phthalaldehyde, TOF-SIMS was performed. This analysis further re-affirmed the hypothesis of phthalaldehyde reacting to form an aromatic ester after depolymerization upon EUV exposure.



Figure S 2- ¹H-NMR- Spectra of un-exposed regions of PA-25 with polymer and proposed side reaction structures labelled with peak shift locations.



Figure S $3 - {}^{1}H$ -NMR- Spectra of exposed regions of PA-25 with polymer and proposed side reaction structures labelled with peak shift locations.

3. TOF-SIMS



Figure S 4 – Mass spectrum obtained by TOF-SIMS of EUV exposed and un-exposed PA-25 samples.