Revealing Beam-induced Chemistry using Modulus Mapping in Negative-tone EUV/E-beam resists with and without cross-linker additives

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Understanding fundamental resist chemistry in candidate systems is crucial for the success of next generation lithographies. Here we investigate modulus variation using PeakForce ${ }^{\mathrm{TM}}$ Tapping AFM analysis to probe intermolecular bonding chemistry in a patterned Noria-MAd (methyl-admantane) molecular resist (Fig. 1). The base resist is mixed with varying amounts ( $0-20 \%$ by weight) of oxetane functionalized Noria to induce cross-linking and increase the material modulus. Previously we reported on the capability to see average modulus changes after exposure as a function of cross-linking concentration. ${ }^{1,2}$ Here, after having refined our data acquisition process, we show distinct modulus changes as a function of dose indicating chemical changes in the resist systems. Figure 2 compares modulus Noria-MAd with 0,5 , and $10 \%$ cross-linker addition over a large dose range. Resists were exposed in a 100 keV electron beam and modulus measurements are shown for both post-exposure (Fig 2a) and post-development (Fig. 2b). Figure 3 shows the modulus contrast curve and thickness contrast curves plotted together for the three resist system. Modulus continues to change far after the material becomes insoluble but then saturates. This is an indicator of deprotection changes in the system. The important implication both for modulus and swelling will be discussed.

In addition, we looked at patterned features as a function of dose for EUV and E-beam exposures. By biasing e-beam features, we increase the center dose of the features. Depending on the dose to pattern relative to the modulus saturation point, this can increase the modulus over unbiased features. E-beam and EUV patterns will be compared down to 20 nm half-pitch resolution.
[1] P.K. Kulshreshtha, K. Maruyama, S. Kiani, D. Ziegler, J. Blackwell, D. Olynick, P.D. Ashby, in: SPIE Advanced Lithography, International Society for Optics and Photonics, 2013, pp. 86810O-86810O86811.
[2] P.K. Kulshreshtha, K. Maruyama, S. Kiani, S. Dhuey, P. Perera, J. Blackwell, D. Olynick, P.D. Ashby, in: SPIE Advanced Lithography, International Society for Optics and Photonics, 2013, pp. 86820N-86820N-86810.


Figure 1: Noria Molecule and adamantane functional (R) group. The adamantane group is removed during acid deprotection. Mixing this system with oxetane functionalized Noria allows intermolecular cross-linking.


Figure 2. A) Modulus after exposure, before development. Note the material modulus of the unexposed resist is not expected to be significantly different between the systems. At high doses, the 20\% oxetane mixture has a higher modulus than the other two materials. B) Modulus after development. Clear differences are apparent in all three samples. Modulus contrast increases with dose because more deprotection occurs-these deproctecting groups are rinsed away in the development--allowing better intermolecular bonding between neighboring Noria. The effect of cross-linker additives on modulus is also clearly apparent.


Figure 3. Modulus and contrast curves for 0,5 , and $20 \%$ oxetane additions. Curves show significant chemical changes occur after the film reaches full thickness, even in the non-crosslinking system, $0 \%$ oxetane sample. Insets show patterned features for oxetane samples. The lightening bolt shows the relative position on the dose curve. The $20 \%$ oxetane sample has less pattern collapse for the same feature size.

