

“Resolving” the Mysteries of Electron Beam Resist Exposure and Development

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Scientific Thrust Area

In the Nanofabrication Facility at the Molecular Foundry, one of the main thrusts is to enable new nanoscience with single digit nanofabrication (sub-10 nm patterning). Despite considerable efforts, patterning sub-10 nm features is still not routine. In electron beam lithography, there is substantial evidence that electron beam resist resolution is often limited by the development conditions (due to contrast, swelling, and collapse) and not beam size. For instance, Fujita et. al.¹ demonstrated the minimum resolvable feature of 10 nm in calixarene was independent of e-beam energy (varied from 10 to 50 keV) and found collapse was dose dependent. Yasin, et. al.² showed better line acuity is achieved with ultrasonic development. Furthermore, chemical reactions induced by the beam during exposure can extend far beyond the electron scattering range and limit resolution.³

Research Achievements

We have combined numerous techniques to study the exposure and development chemistry of electron beam resists. We begin to reveal mechanisms responsible for resolution, where the limits lie, and how to best utilize e-beam resists for directed self assembly. In our studies of hexaacetate p-methyl-calix[6]arene, a high resolution negative macro-molecular resist (6 nm isolated lines have been demonstrated²), we investigate the interplay between thermodynamics and kinetics during development and the effects on nanoresolution. Using solubility parameters and measuring the Hansen Solubility Sphere (HSS) for calixarene, we have estimated the Flory-Huggins interaction parameter, χ , for calixarene and numerous developers (Fig. 1). Using this, we unravel how development contrast evolves and the contributions to pattern swelling and collapse (two of the biggest resolution limiters). Long development times were investigated to elucidate kinetically versus thermo-

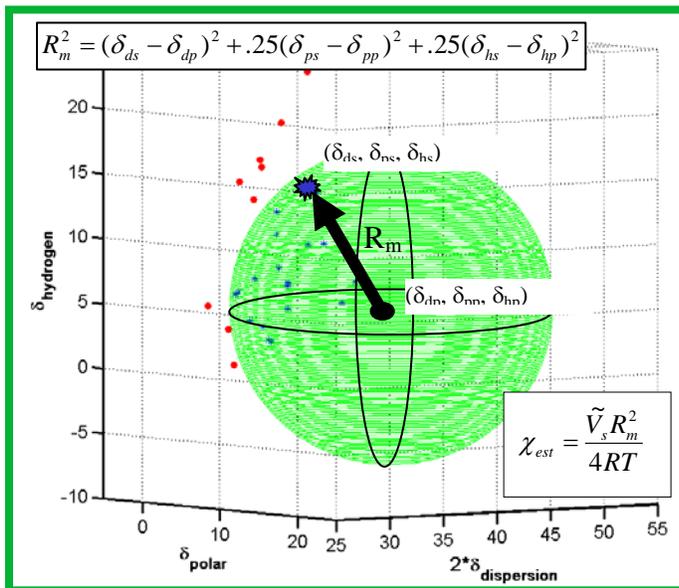


Fig. 1. Hansen Solubility Sphere for calixarene. Determined empirically by looking at calixarene solubility in several solvents (red dots, insoluble, blue dots, soluble). Any solvent with a solubility parameter inside the sphere will dissolve calixarene. Allows estimation of the Flory-Huggins parameter, χ , for all solvents.

dynamically driven behavior. Contrast is higher at lower development times because low molecular weight material is trapped in the beam networked matrix. Using atomic formic microscopy (AFM), we probe calixarene immersed in solvent developers

(Fig. 2). One of the crucial findings is that the low molecular weight material trapped in the matrix contributes significantly to swelling and limits resolution (this is driven by lowering of the Gibbs free energy through the entropic term).

In studies of Hydrogen Silsesquioxane (HSQ), an inorganic resist system, we have investigated chemistry induced by the exposing beam. With Raman spectroscopy and electron-beam induced desorption, we identified a beam exposure mechanism. The Si-H₂ peak present in the Raman spectra in combination with the e-beam induced desorption of silane, reveal that cross-linking of HSQ occurs via a redistribution reaction (Fig. 3). In this reaction, hydrogen removed from an HSQ cage bonds with silicon on a nearby cage. This breaks a Si-O bond. The oxygen dangling bond then bridges to the neighboring cage where the hydrogen was lost from a silicon atom. This cross-links the two cages and contributes to the formation of a network. As the system becomes more cross-linked, it becomes more resistant to attack by the aqueous base developer. Currently, we are studying the mechanism of aqueous base development of HSQ.

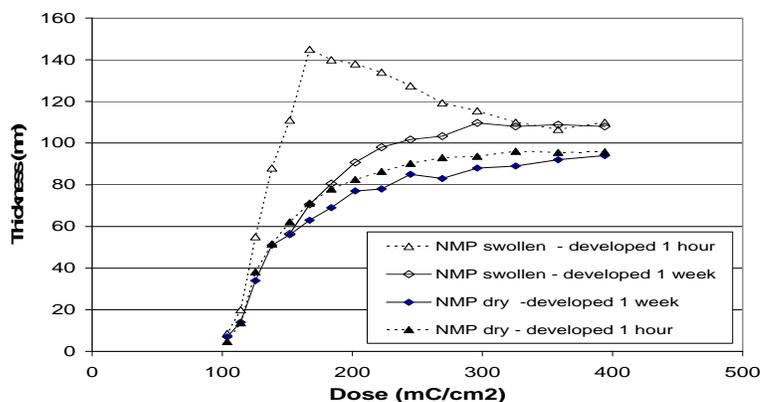
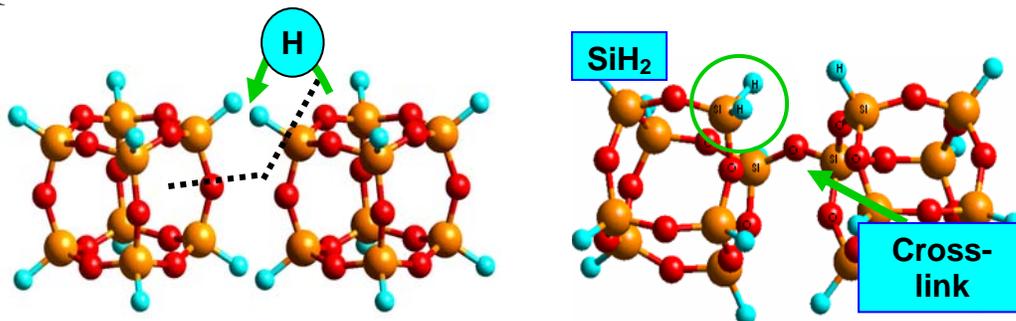


Fig. 2. Chart showing AFM measured thickness of exposed calixarene during development (swollen) and after removing the solvent (dry). The small amount of un-networked material (we know it is un-networked because it is removed with long development times) present in the 1 hour development versus the 1 week development contributes significantly to the resist swelling.

Fig. 3. Networking of HSQ through the redistribution reaction.



Future work

Using these findings, techniques, and our developed expertise, we will investigate new resist materials for single digit nanoresolution, improved process integration (i.e. etching resistance), directed self-assembly, and as active materials. For instance, a user project is underway which uses the techniques developed at the Molecular Foundry to probe new inorganic resists based on ZrO₂ and HfO₂. An internal project is starting to study patterning of nanoparticle embedded calixarenes.

References

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- ² Shazia Yasin, D. G. Hasko, and F. Carecenac, *J. Vac. Sci. Technol. B* **19** (1), 311 (2001).
- ³ Deirdre L. Olynick, J. Alexander Liddle, Alexei V. Tivanski et al., *Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures* **24** (6), 3048 (2006).

Publications

Deirdre L. Olynick, Paul Ashby, Mark D. Lewis, Haoren Lu, J. Alexander Liddle and Weilun L. Chao, "The link between nanoscale feature development in a negative resist and the Hansen Solubility Sphere" Accepted Journal of Polymer Physics 2009