

X-rays, Electrons and Lithography: Fundamental Processes in Molecular Radiation Chemistry

The interaction of ionizing X-ray radiation with molecular resist films in extreme ultraviolet lithography (EUVL) is fundamentally different from the resonant photochemistry of deep ultraviolet lithography, and is different again from the electron-resist interactions of electron beam lithography (EBL). High-volume semiconductor manufacturers are now making significant investments in EUVL and getting ready for pilot production, but the sensitivity and resolution of EUV photoresists fall short of targets. A molecular scale understanding of radiation chemistry is required to design resist materials that efficiently absorb X-ray energy, and then harness that energy to drive chemical transformations leading to solubility changes and ultimately to pattern transfer.

Molecular relaxation is critically important for understanding and optimizing EUVL resist systems.¹ The most-strongly-bound molecular or atomic orbitals that can be excited by EUV x-rays have the highest photo-ionization probability. This is in contrast to EBL, where the most weakly bound orbitals have the highest impact-ionization probability. The initial photoelectrons will have relatively low energy, and molecules will be left with a significant amount of residual internal energy. Relaxation generates additional secondary electrons, followed by molecular fragmentation into radicals and radical ions. Relaxation processes are especially important when resist sensitivity is increased by incorporating high EUV cross-section atoms with deep-valence orbital binding energies between 30 and 90 eV.

It is difficult to directly investigate the EUV and EBL reaction cascades in condensed systems such as thin-film photoresists and to understand fundamental reaction mechanisms. I will discuss experimental gas-phase investigations at the Advanced Light Source now being carried out by a multi-disciplinary team of LBNL scientists from the Molecular Foundry, the ALS Chemical Dynamics Group and the Center for X-Ray Optics. Experiments on a series of model molecules, halogenated methyl phenols, which are analogs for the polymer side-chains now used in deep UV photoresists, show the importance of molecular structure on the photo-absorption cross-sections. In one set of experiments a velocity-map imaging (VMI) spectrometer was used to measure secondary electron yields and energy distributions as a function of x-ray energy. In another set of experiments a time-of-flight (TOF) mass spectrometer was used to measure molecular fragmentation patterns as a function of incident x-ray or electron energy. We are also carrying out theoretical studies of molecular radiation chemistry processes.²

[1] D. F. Ogletree, "Molecular Excitation and relaxation in extreme ultraviolet photoresists", in Materials and Processes for Next Generation Lithography, eds. Alex Robinson and Richard Lawson, Elsevier Frontiers of Nanoscience, Vol. 11, 2017. Doi: 10.1016/B978-0-08-100354-1.00002-8.

[2] The importance of inner-shell electronic structure for enhancing the EUV absorption of photoresist materials. Kristina D. Closser, D. Frank Ogletree, Patrick Naulleau and David Prendergast (in review).