

Chemical changes during exposure of ZEP 520A electron beam resist
David A. Czaplowski, Leonidas E. Ocola, and Derrick C. Mancini
Argonne National Laboratory, Argonne, IL, USA

Fabrication of nano-scale systems and devices can be done using electron beam lithography, which has been used to create unique isolated patterns with dimensions in the tens of nm [1]. After the patterns are made in e-beam resists, typically, a lift-off process is performed to create isolated metal features to be used as etch masks. Ideally, the resist would be used as an etch mask to pattern the subsequent layers to reduce processing steps and to preserve surfaces. E-beam resists, however, typically have poor selectivity relative to the underlying materials in reactive ion etch (RIE) processes.

Recently, a post exposure curing method involving heat and UV treatment of ZEP 520A, an e-beam resist, has shown improvement in RIE selectivity of the resist [2]. ZEP 520A is a copolymer of chloro-methacrylate and methyl-styrene [3]. The heat and UV process was developed after the observation that scanning electron microscope (SEM) imaging of the resist improved the RIE selectivity to SiO₂ in subsequent processing steps. In Fig. 1, two trenches, patterned in ZEP and then etched into the underlying SiO₂ layer, have significantly different shapes and definition. After patterning of the ZEP, the feature on the right was imaged by SEM. Following the SiO₂ RIE, the differences between the two channels is evident. Even though they have been fabricated in close proximity, the changes induced in the resist by the second exposure to electrons from SEM imaging created a very different structure after etching.

In order to understand the chemical changes that enhance the etch selectivity of the resist during electron beam exposure, we used Fourier transform infrared (FTIR) (Fig. 2) and Raman (Fig. 3) spectroscopy to study the resist. In the FTIR spectra, a peak near 1750 cm⁻¹ decrease in intensity as the electron dose is increased. Peaks in the range between 1675 and 1750 cm⁻¹ are associated with carboxyl group activity. It is possible that multiple carboxyl group configurations are present in the resist thin film that produce 2 main peaks and a side peak just below 1700 cm⁻¹. The carboxyl configuration near 1750 cm⁻¹ is the most susceptible to radiation damage from the electron beam and therefore its intensity decreases with higher dose. The Raman spectra show a main peak near 1600 cm⁻¹. Peaks near 1600 cm⁻¹ are associated with phenyl groups in the styrene copolymer. As the electron dose is increased, a side band near 1625 cm⁻¹ forms and increases. The decrease in intensity of one of the peaks associated with carboxyl groups along with an increase in intensity of a peak associated with phenyl groups suggests that crosslinking occurs from the scissioned polymer segments of carboxyl group to a phenyl group. From previous work, crosslinked polymers tend to have higher RIE selectivity.

After identifying the chemical changes that occur in the ZEP resist, it may be possible to propose a new resist chemistry that provides better etch selectivity combined with the high sensitivity of the ZEP resist. A more detailed analysis of the carboxyl group configurations susceptible to electron beam damage will be discussed.

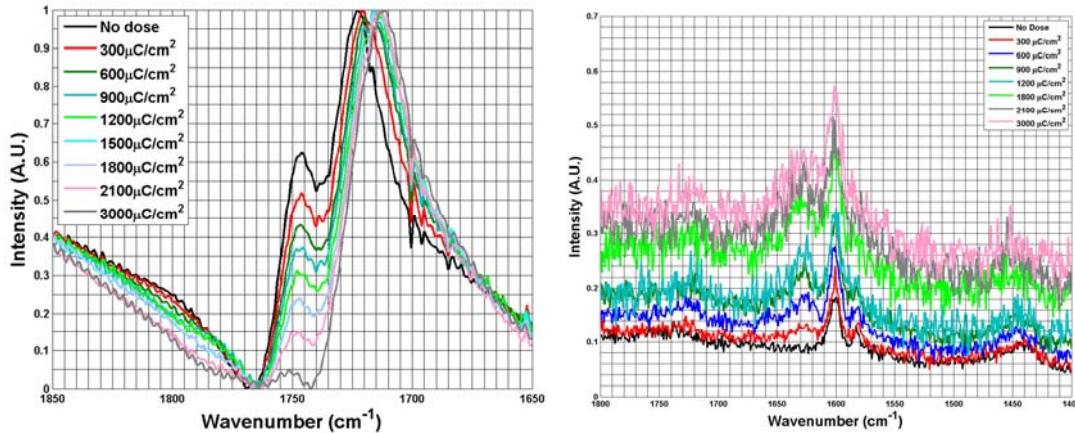
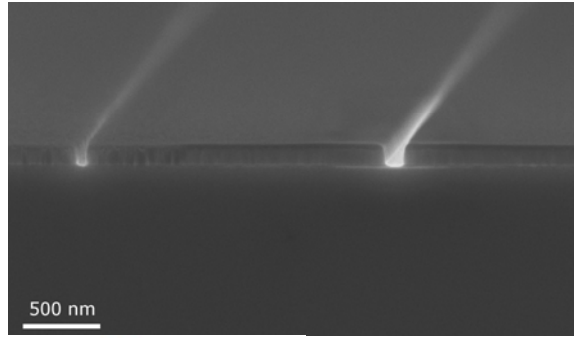


Figure 1 Scanning electron micrograph of two trenches etched into SiO₂. The resist for the trench on the right was exposed to a secondary electron beam before RIE. The trench on the left was processed without resist modification. The shape and definition of the two trenches are significantly different.

Figure 2 Infrared spectroscopy of the resist after various electron doses. IR analysis shows significant change in the vibrations associated with the carboxyl group. We suspect that the Chlorine opposite the carboxyl group scatters electrons, causing polymer cleavage in the local area. This cleavage breaks the added mass to the carboxyl group, causing a shift lower in wavenumber.

Figure 3 Raman spectroscopy of the resist after various electron doses. Raman analysis shows significant changes in the vibrations associated with the styrene group. As the dose is increased, cross-linking occurs in the resist causing some of the phenyl groups to add mass. The added mass causes a peak to develop at higher wavenumber.

[1] L. E. Ocola, and A. Stein, *J. Vac. Sci. Technol. B* **24**, 3061 (2006).

[2] D.A. Czaplowski, D.R. Tallant, G.A. Patrizi, J.R. Wendt, and B. Montoya, *Journal Vacuum Sci. Tech.*, B **27**, 581, 2009.

[3] T. Nishida, M. Notomi, R. Iga, and T. Tamamura, *Jpn. J. Appl. Phys.* **31**, 4508, 1992.

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.