Investigations into the Exposure Mechanism of Hydrogen Silsesquioxane Resists using Infrared Spectromicroscopy

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Since its initial discovery[1] as a high-resolution negative-tone electron-beam resist, hydrogen silsesquioxane (HSQ) has become popular for direct-write e-beam, extreme ultraviolet (EUV) and nanoimprint lithographic (NIL) applications. HSQ is attractive as a resist for a variety of reasons including demonstrated high-resolution down to 12.5 nm half-pitch gratings,[2] sensitivity comparable to Zeon corporation's ZEP-520 or polymethyl methacralate (PMMA), and excellent dry etch pattern transfer characteristics. Unfortunately, a number of authors have noted a degree of instability and irreproducibility with electron beam exposure of HSQ,[3,4,5] with one group[5] finding a dependence on both the area exposed and the e-beam writing algorithm.

Using scanning transmission x-ray microscopy (STXM), we recently observed in e-beam latent images of HSQ (exposed but not developed) a surprising migration of the e-beam induced reaction front outside the patterned regions.[6] It is not yet certain whether the extended reaction front is due to diffusion of some radical species or to a chain reaction cross-linking chemistry. In this paper we employ spatially resolved Infrared Fourier Transform Spectromicroscopy (FTIRSM) to investigate the network conversion both within and outside of patterned features. The FTIRSM probe is on the order of 8 μm. Films of HSQ 250 nm thick were prepared on 100 nm thick Si_3N_4 membranes. The HSQ was exposed with a set of two 50 μm wide stripes using a 100 keV electron-beam lithography system (Leica VB6) with a 6.5 nm FWHM probe. The spacing between these features was varied from 25, 50 and 100 μm with e-beam doses between 1 and 6 mC/cm^2.

Figure 1 shows reference spectra and a difference spectrum between exposed and unexposed HSQ in the infrared wavelength regions of high chemical contrast. Figure 2 shows the IR transmission dependence on e-beam feature spacing for three IR vibrational bands. This can be seen in the center panel as a signal dip for the largest feature spacing (cyan colored line) which is significantly larger than that for the smaller feature spacings. The signal dip level corresponds to the background level on the outer edges of the exposed lines. The first and third panels show a signal between features that never reaches background levels, i.e. different infrared modes in HSQ exhibit different dependencies on feature spacing. The infrared results confirm the observations by STXM, namely that the e-beam induced chemical changes extend spatially well beyond the patterned region. In this paper we will present futher details on HSQ chemical changes during electron-beam exposure as a function of feature density and area.

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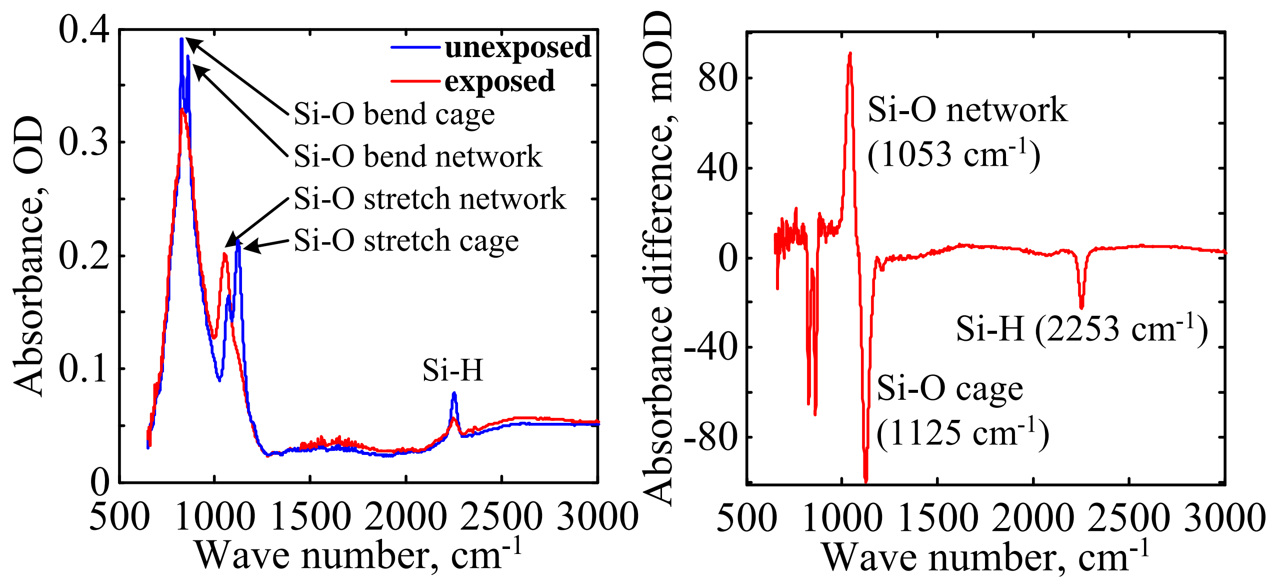

Figure 1. Infrared spectra of HSQ samples taken before and after electron beam exposure. Absorbance spectra (left), difference spectrum (right).

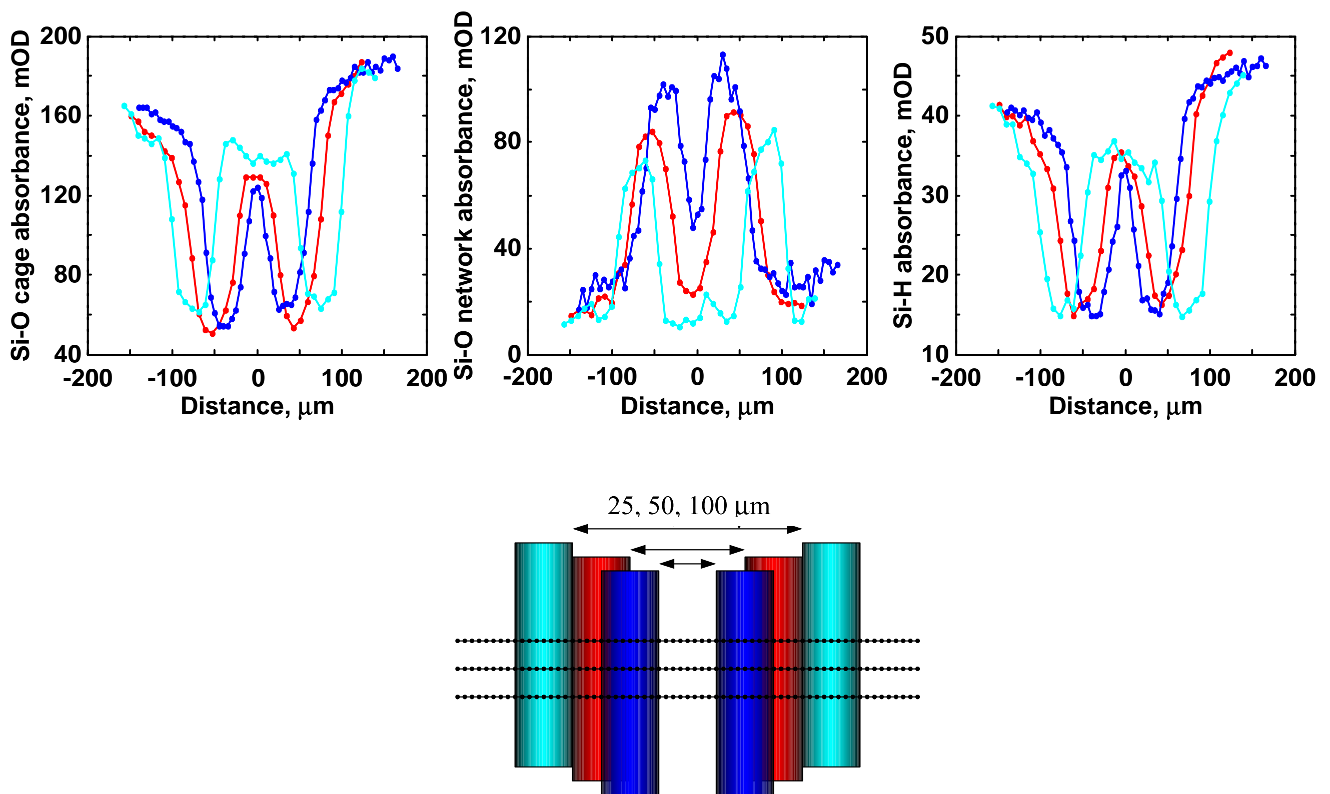

Figure 2. Changes in infrared transmission on patterned, undeveloped HSQ lines and as a function of spacing between two 50 micron wide exposed rectangles (25, 50, 100 um spacings, blue, red, cyan, respectively). Graphs from left to right: Si-O cage stretching mode. Si-O network stretching mode, and cage Si-H stretching mode.