An alternative electron beam exposure mechanism for hydrogen silsesquioxane – a Raman and FTIR study

D. L. Olynick, A. Schipotinin, S. D. Dhuey, S. Cabrini and P. J. Schuck
Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

FTIR and Raman spectromicroscopy have proven to be a powerful techniques in the study of lithographic resist systems and polymer systems in general.[1] FTIR is a more mature technique and well characterized FTIR spectra are available for many systems. However, even under the best circumstances (a diffraction limited spot with coherent light from a synchrotron), spatial resolution for FTIR is limited to the approximately 8 μm. Raman spectroscopy has a huge spatial resolution advantage over FTIR, with the possibility of diffraction limited spots below 500 nm. Thus, Raman has been used to probe dynamic processes such as diffusion and dissolution in polymer systems.[1] Ultimately, using Raman techniques in combination with field enhancing plasmonic devices such as bowtie nanoantennas,[2] we can beat the diffraction limit and probe resist chemistry as a function of processing with sub-20 nm spatial resolution. Towards that end, we are characterizing e-beam resists using diffraction limited Raman spectroscopy (HeNe wavelength = 632.8 nm, diffraction limited spot verified at ~300 nm) with a focus on hydrogen silsesquioxane (HSQ).

For these studies, we have investigated HSQ using Raman spectroscopy as a function of bake temperature, substrate, and electron beam exposure dose.   Silicon, silicon nitride, fused silica and quartz were all investigated as substrates for compatibility with HSQ. Fig. 1 A and B show HSQ Raman spectra as a function of bake temperature on silicon and quartz (~500 nm HSQ, 1 hour bake in air). Fig. 1 C shows FTIR spectra of the identical HSQ-on-silicon sample, probed in Fig. 1 A. The FTIR spectra shows changes typical of HSQ when thermally treated;[3] the Si-H peak at ~2256 cm^{-1} and the 1070 cm^{-1} (Si-O-Si stretch cage) peaks decrease in strength, while the 1132 cm^{-1} increases (Si-O-Si stretch network). The intensity of the 830 cm^{-1} peak increases relative to the 863 cm^{-1} peak (O-Si-H bend), again due to networking. In the Raman spectra, both substrates (as well as fused silica) replicate the FTIR peak behavior at ~2256 and thus this peak can be used as an indicator of HSQ film quality.   Most of the other peaks in the silicon spectra are masked by the background Raman signal from the silicon. However, the quartz substrate clearly shows several peaks from the HSQ which change with thermal treatment. Of particular interest is a peak at ~2200 in the 300 and 400 ° C baked samples which is attributed to the SiH_2 bond. This peak indicates a redistribution reaction involving 3 silicon atoms where one silicon will end up bonded to 2 oxygens and 2 hydrogens; the two other silicons will bridge via oxygen across neighboring cages to further network the system (with the third silicon bonded to three oxygen atoms). Fig. 3 shows Raman spectra of HSQ on silicon for unexposed (no bake) and exposed but undeveloped HSQ films (170 nm thick) at three exposure doses (1, 2.5, 6 mC at 100 keV). Again, the peak around 2200 cm^{-1} is present in the exposed samples. Thus, cross-linking by electron beam appears to occur, at least in part, by a redistribution reaction and is not necessarily dependent on the presence of hydrolyzed bonds as proposed by Namatsu, *et. al.*[4] This mechanism may provide new insights into the changing dose requirements for HSQ as a function of area[5,6] and will be discussed.

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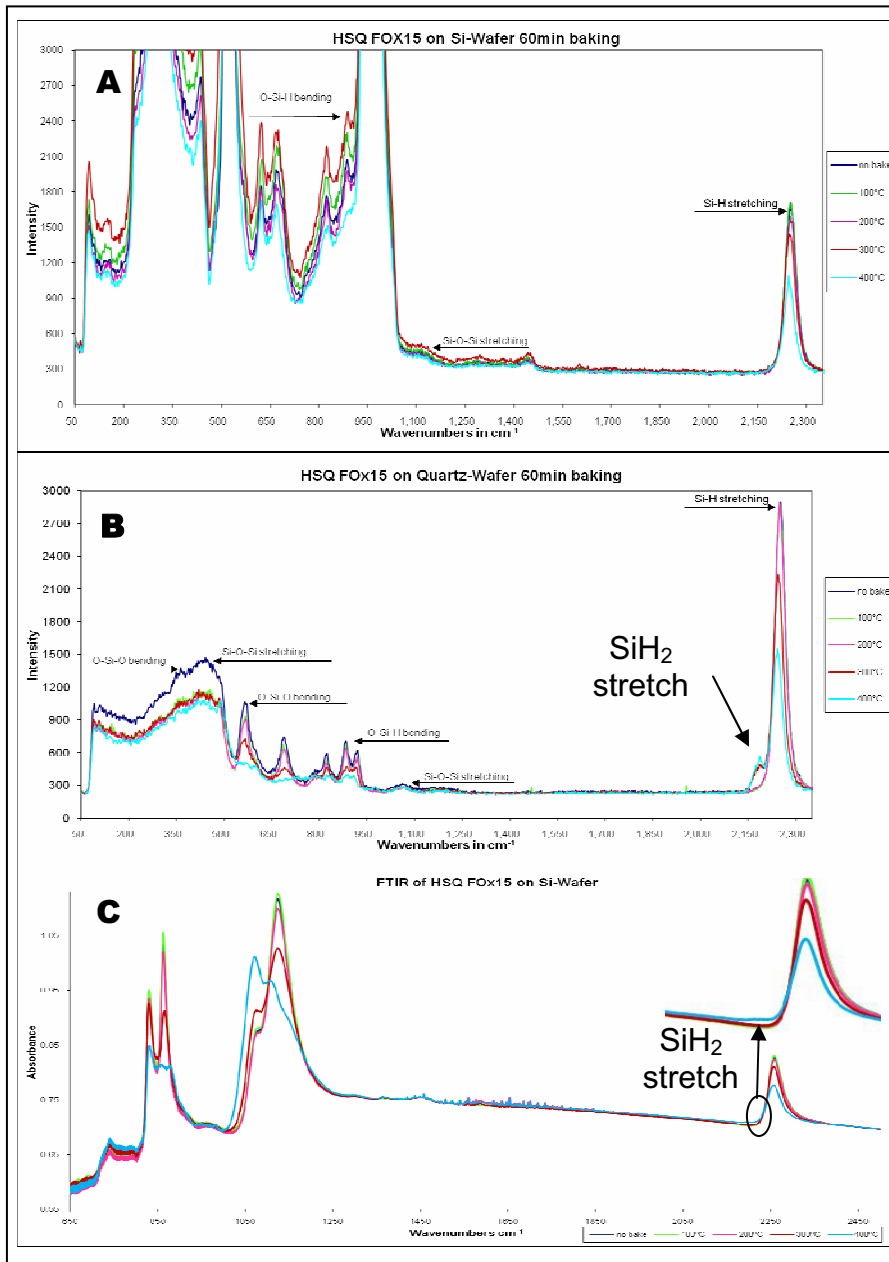
Fig. 1. Raman Spectra of HSQ on A) Silicon and B) Quartz and C) FTIR on silicon as a function of thermal treatment. FTIR spectra is typical of thermally treated HSQ. In the Raman spectra, Si-H stretching at ~2256 cm^{-1} is apparent on both samples and is a good peak to track film changes. Silicon background obscures lower wave number peaks in Raman spectra while quartz substrates allow observation of peaks above 500 cm^{-1}. A peak at ~2200 can be seen on the quartz sample which we attribute to SiH$_2$ from a redistribution reaction.
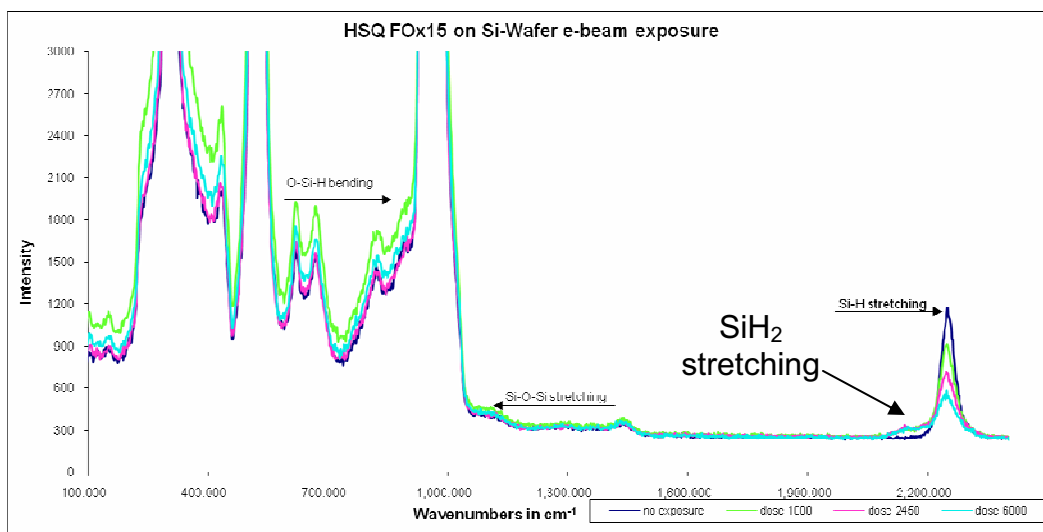

Fig. 2. Raman spectra of HSQ on silicon as a function of e-beam exposure dose at 100 keV. Note appearance of SiH$_2$ stretching mode.