Pattern exposure order dependence in hydrogen silsesquioxane

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**Motivation**
Pattern order dependence is observed and characterized in electron beam lithography (EBL) exposed hydrogen silsesquioxane (HSQ) resist. Previously, HSQ has been reported to have a time delay effect\[^1\] which could auto-correlate to pattern order depending on the time required to expose the pattern. However, this observed effect is different, whereby the HSQ is sensitive to exposure order and location, is repeatable over time, and not a function of delay time. Previous work\[^2\]\[^3\] has identified pattern order dependence, but the mechanism is yet to be fully explained.

**Materials and Methods**
- 35 mm square silicon substrates
- 6% HSQ (XR-1541)
- spin coat at 5000 RPM, 2000 RPM/sec, 60 sec
- ~100 nm film thickness
- immediately exposed, no baking
- 100 kV EBL, 2 nA beam current
- doses 100 – 800 uC/cm\(^2\).
- MF-319 (2.3% TMAH) develop for 70 sec, followed by DI water rinse for 60 sec.

**Characterization**

- Comparing resist height vs. exposure dose of 1st exposed square to adjacent square of the right pattern from Fig 1.

Figure 4: comparing resist height vs. exposure dose of 1st exposed square to adjacent square of the right pattern from Fig 1.

- Pattern order dependence is not observed in PMMA, indicates a chemical mechanism distinct to HSQ.

Figure 5: Pattern order dependence is not observed in PMMA, indicates a chemical mechanism distinct to HSQ.

- Comparing unbaked HSQ to pre and post exposure 250 deg C, 2 min hot plate baked HSQ.

Figure 6: Comparing unbaked HSQ to pre and post exposure 250 deg C, 2 min hot plate baked HSQ.

- First exposed square does not have Si-H bond present at 2256 cm\(^{-1}\) Raman spectroscopy wavelength indicating lower H concentration.

Figure 7: Raman spectroscopy. First exposed square does not have Si-H bond at 2256 cm\(^{-1}\).

**Observation of Order Dependence**

Figure 1: Top row shows controlled pattern exposure order of 10 um squares spaced by 1 um starting with gray square. Bottom row shows resulting SEM images of HSQ.

**Atomic Force Microscopy**

Figure 2: AFM scan of same HSQ pattern from Fig. 1 confirming height difference.

**Nanodot Array**

Figure 3: SEM image of 27 nm dots on 100 nm pitch in 10 um arrays in same controlled order. dose = 5,000 uC/cm\(^2\), develop 25% TMAH 30 sec

**Conclusions**
The following are new conclusions of this work compared to previous work.
- the effect is not observed in PMMA, and thus indicates a chemical mechanism distinct to HSQ
- the effect is observed at both micron scale (10 um squares) and nanometer scale (27 nm dots on 100 nm pitch) binary lithography
- the presence of heat before or after exposure is not responsible for the lower observed height, and therefore the effect cannot be caused by local beam heating
- the first exposed square does not have the Si-H bond present at 2256 cm\(^{-1}\) Raman spectroscopy wavelength indicating lower H concentration.

**References**
\[^1\] D.A. Westly, J Vac Sci Technol B 29 (2011)