Dry Development of HSQ in Chlorine Plasma

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Hydrogensilsesquioxane (HSQ) has become a popular resist for electron-beam lithography (EBL). Recent advancement in high-temperature TMAH and salty development enabled half-pitch down to 4.5nm in HSQ [1]. However, high resolution features demands extremely thin (10nm) resist, and dense, high-resolution features may be limited by surface tension during the drying process of the wet development. Furthermore, it is suggested that the wet development process may stop shortly after the initial development.

Here we propose a dry development process for HSQ using Chlorine based high-density plasma etch. HSQ is a compound formed by silicon, oxygen, and hydrogen atoms. Upon electron beam bombardment, HSQ can be converted to SiO_2, or at least the hydrogen concentration will be significantly reduced. As SiO_2 is thermodynamically more stable than the etch product formed by Si and Cl_2 ($SiCl_4$), e-beam exposed HSQ will be resistant to Cl_2 based plasma etch. In practice, with the kinetic energy associated with reactive-ion-etching (RIE), exposed HSQ will be slowly etched by Cl_2 plasma.

We propose that unexposed HSQ, due to the presence of hydrogen atoms, will facilitate the removal of HSQ under Cl_2 plasma. A very rudimental modeling of the etching process might be the following exothermic process:

$$SiO_2 \text{ (solid)} + 2H_2 \text{ (gas)} + 2Cl_2 \text{ (gas)} \rightarrow SiCl_4 \text{ (gas)} + 2H_2O \text{ (gas)}$$

We note, however, that this model, treating the HSQ as a mixture of solid SiO_2 and H_2 gas, is not strictly correct.

To test our hypothesis, we spun HSQ resist of ~15nm thickness and exposed it with the Vistec VB6 EBL system. The exposed HSQ was loaded into the Panasonic E620 ICP etcher and was etched with Cl_2 plasma (50 sccm flow rate) at a pressure of 0.28Pa. The etch rate was 1.3~1.4nm/min. The selectivity was 6:5 for unexposed/exposed HSQ, which is low at this moment.

Despite the low selectivity, various patterns have been achieved using dry development with reasonable contrast (Fig. 1 and 2). Figure 3 shows L shapes down to 40nm pitch.

We plan to apply the dry development to a bilayer resist process, where HSQ is placed on top of an organic layer, such as SU8, that can be etched in Cl_2 with high selectivity to either exposed or unexposed HSQ. Another approach is to try BCl_3 chemistry, which may use the following chemistry when hydrogen is present:

$$3SiO_2 \text{ (solid)} + 3H_2 \text{ (gas)} + 2BCl_3 \text{ (gas)} + 3\, Cl_2 \text{ (gas)} \rightarrow 3SiCl_4 \text{ (gas)} + 2\, H_3BO_3 \text{ (gas)}$$

If few hydrogen atoms are present, the product of Boron will be B_2O_3, which is much less volatile, thus larger selectivity might be achieved for exposed/unexposed HSQ.

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References:

[1] Yang, J. K. W. *et al* J. Vac. Sci. & Technol. B **27**, 2622 (2009)

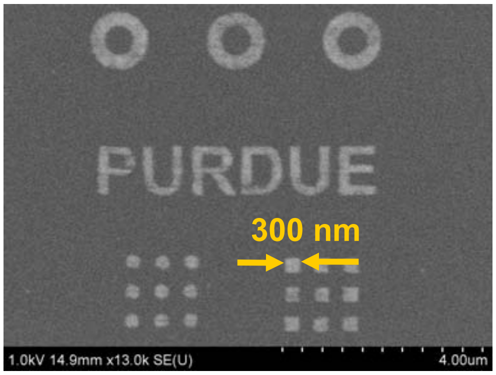

Fig. 1: Rings, dots and the word of "PURDUE" patterned in HSQ via dry development. The remaining HSQ is 3 – 5 nm thick.

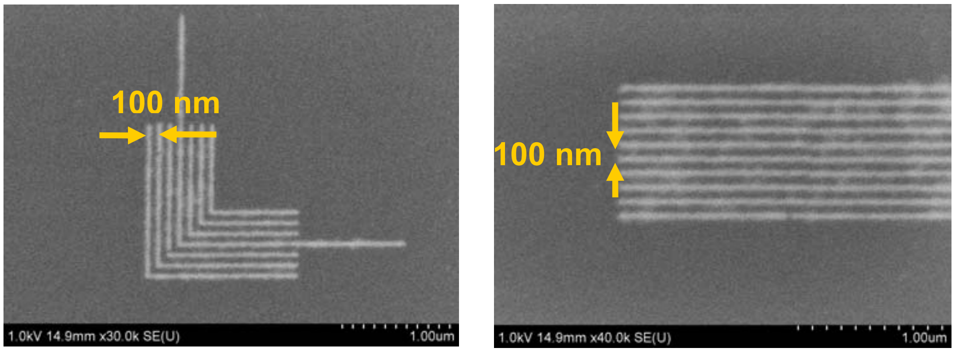

Fig. 2: L shapes and gratings of 100nm pitch in dry developed HSQ.

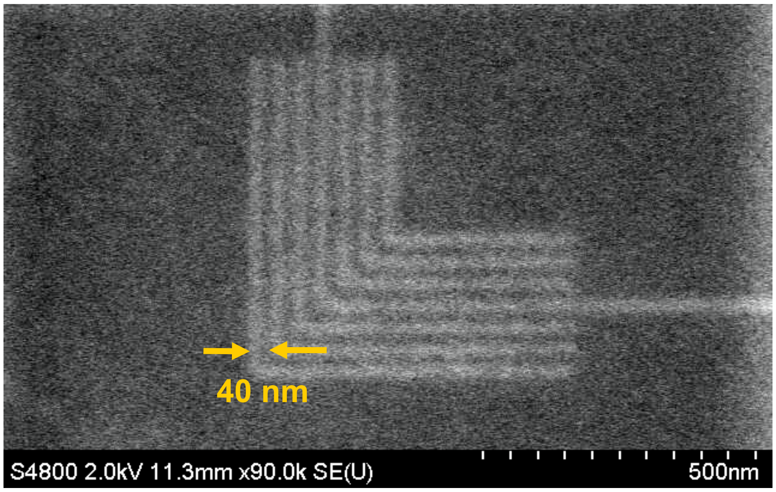

Fig. 3: L-shapes defined in HSQ using dry development. The pitch is 40nm.