Designing Hydrogen Silsesquioxane: Control Over Particle Size, Shelf Life, and Sensitivity

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Hydrogen silsesquioxane (HSQ), a widely used negative resist, is a mixture of monomers, oligomers, and polymers with the empirical formula $(HSiO_{3/2})_n$. Applied Quantum Materials Inc. (AQM) is a supplier of solid- and solution-phase HSQ. AQM's solid HSQ possesses an indefinite shelf life when stored in accordance with handling guidelines. The shelf life of HSQ decreases when dissolved. To improve solution shelf life, nanolithography processing, and ease of handling, AQM has designed, prepared, and commercialized well-defined HSQ variants.

Light scattering methods were employed to interrogate the make-up of HSQ solutions and the resulting number-weighted particle diameters are summarized in Table 1. A competitor's HSQ was examined for comparison. The particle diameters for AQM's HSQ-A and -B are 45 and 16% smaller than the competitor's HSQ, respectively. The particle diameters for AQM's HSQ-C and -D are 67 and 98% larger than the competitor's HSQ, respectively. All batches are being stored at room temperature and monitored over 2 years (i.e., 5 hours, 3 weeks, 3 months, 6 months, 1 year, and 2 years).

Particle size distributions influence HSQ spin curves (Figure 1). Solutions containing larger particles (i.e., HSQ-C and -D) resulted in thicker coatings, while smaller particles (i.e., HSQ-A and -B) produced similar thinner coatings. These differences are related to solution viscosities.

An 80 nm thick layer of HSQ-B, on a Si wafer, was tested using a RAITH150 Two at 30 kV (15 µm aperture). The HSQ was exposed at varying dosages and then developed in MF-319. For 20 by 50 µm rectangles, the threshold and saturation dosages occurred at ~75 and ~300 $\mu C/cm^2$, respectively (Figure 2). Sensitivity, contrast, and feature sizes are being explored with the defined AQM HSQ variants.

Table 1. Number-weighted particle size distribution data.

HSQ	Peak [nm][a]	Distribution [%][b]
A	3.15 (0.40)	12.7
B	4.80 (0.70)	12.2
C	9.60 (1.57)	11.4
D	11.39 (2.02)	12.0
Competitor	5.74 (0.19)	13.3

HSQ was dissolved in an appropriate solvent at a consistent concentration. The bottle was sealed, stored at room temperature, and the solution analyzed at 5 hours. [a]The particle diameter reported (standard deviation in brackets) for the peak was an average of several runs (≥5 runs). [b]The distribution was that at the peak particle diameter.

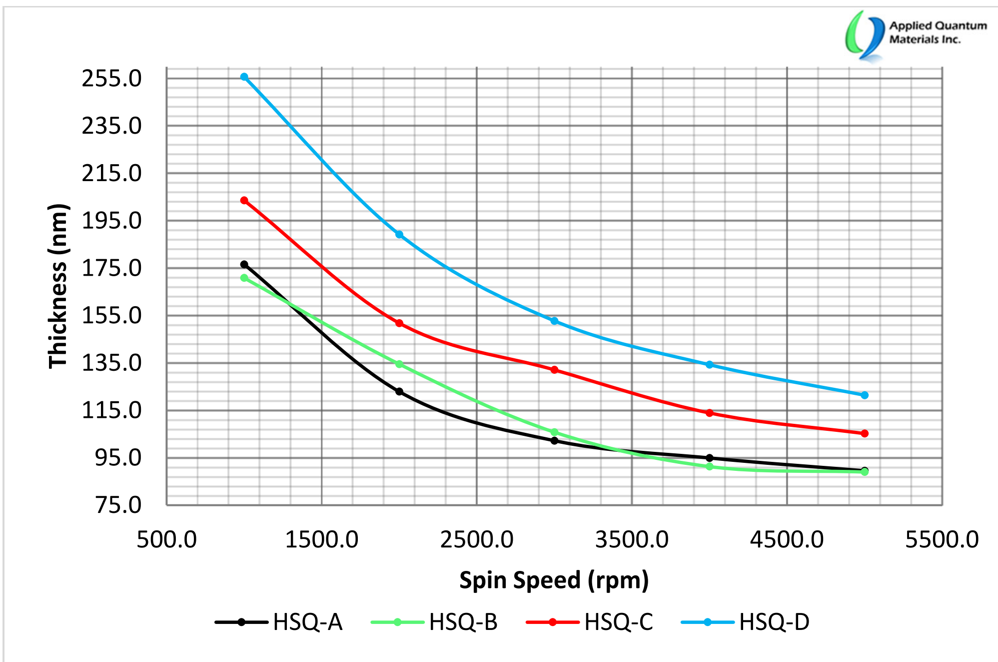

Figure 1. Spin curves of indicated HSQ batches at a consistent concentration. Piranha cleaned, 180 °C prebaked, 10 by 10 mm wafers were coated with HSQ and spun at 1000, 2000, 3000, 4000, or 5000 rpm for 60 seconds total (1 second ramp). A post-apply bake was performed at 80 °C for 3 minutes. The thicknesses of the resists were determined using a Filmetrics® F50-UV.

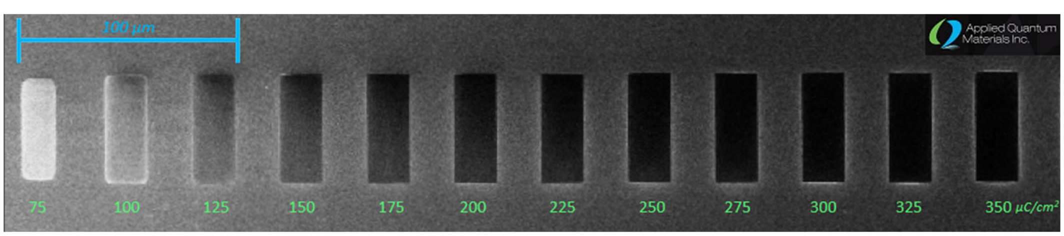

Figure 2. SEM image of dose rectangles formed on an exposed (RAITH150 Two at 30 kV, 15 µm aperture) and developed (MF-319, 90 seconds, deionized H_2O, 60 seconds) ~80 nm thick layer of HSQ-B. The dose rectangles are supposed to be 20 by 50 µm.