In-situ study of rate of hydrogen silsesquioxane dissolution in both alkaline and electrochemical systems

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The fabrication of sub-10 nm pitch structures using electron beam lithography may be limited by the development of the resist material rather than exposure effects.[1] Several groups have reported a correlation between development rate and achievable resolution. Cord et al. suggested that the increase in achievable resolution yielded by adding sodium chloride to the developer was linked to an increased development rate of unexposed hydrogen silsesquioxane (HSQ).[1] Furthermore, Lee et al. showed that a layer of Si^{4+} built up on the HSQ surface during development in tetramethylammonium hydroxide. Once the buildup of siloxane reached a certain thickness, development stopped.[2] In order to better characterize the development of HSQ, we used a quartz crystal microbalance (QCM) to study its rate of dissolution. We used this technique to determine the development rate in salty developer solution (0 – 20% NaCl in 1% NaOH) and using electrochemical development techniques (0 – 2.5 V in 1% NaOH).

The development rates were measured by spinning HSQ directly onto a quartz crystal resonator then developing in a QCM microfluidic module. The rate at which HSQ dissolved into solution was determined by measuring the change in the crystal's resonance frequency, which is proportional to the change in its mass. When NaCl was added to 1% NaOH developer solution, the development rate increased from 6 nm/s with 0% NaCl to 9 nm/s with 20% NaCl (Figure 1a). Similarly, when a positive electric potential was applied to the crystal during development, the rate increased from 5.5 nm/s with 0 V to 9 nm/s at 2.5 V (Figure 1b).

Finally, a 100-nm thick film of HSQ was partially cross-linked in an O_2 plasma asher then developed in the QCM flow module with 1% NaOH solution. Because partially cross-linked HSQ develops much more slowly than freshly spun HSQ, we could directly observe how the development rate changed as electric potentials were applied and removed from the crystal. When 2.5 V was applied to the crystal, the development rate sharply increased. When the potential was shut off, the development returned to its original rate (Figure 2a). An increase in development rate was also observed by comparing the amount of HSQ removed between features patterned using a Raith 150 electron beam lithography tool after 45 s of development with and without an electric potential (Figure 2b).

The increased development rate caused by both the addition of salt ions and a positive potential suggest that the rate may be limited by a build-up of negative charge on the HSQ as proposed by Cord and Yang et. al. in 2009.[1] Understanding the self-limiting nature of HSQ development will allow us to design a development system that stretches these limits in order to achieve higher resolution structures.

1. Cord, B., J. Yang, et al. (2009). "Limiting factors in sub-10 nm scanning-electron-beam lithography." JVSTB. 27(6): 2616.
2. Lee, H.-S., J.-S. Wi, et al. (2009). "Two-step resist-development process of hydrogen silsesquioxane for high-density electron-beam nanopatterning." JVSTB. 27(1): 188-192.

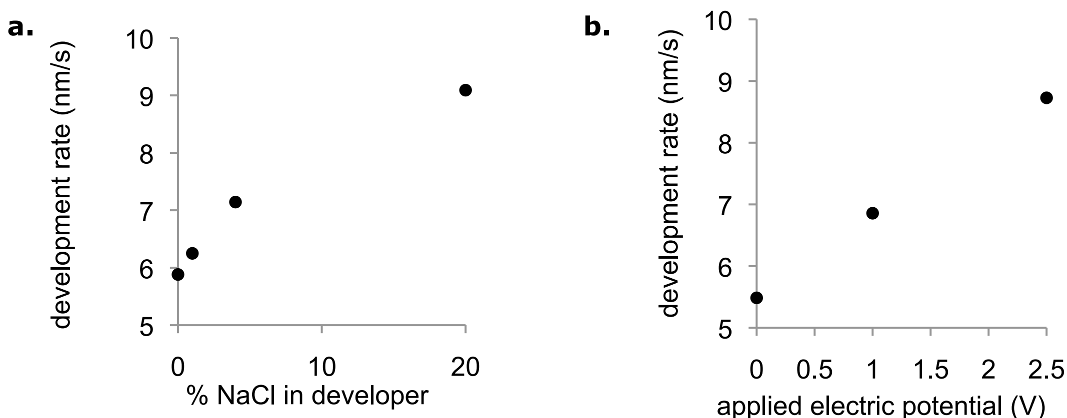

Figure 1. The development rate of HSQ in salty developer and electrochemically-enhanced developer was determined with a Quartz Crystal Microbalance. **a)** 96 nm of HSQ resist was spun onto a gold-plated quartz crystal. The crystal was mounted in a QCM flow module and developed with 1% sodium hydroxide mixed with varying concentrations of sodium chloride. The development rate increased as the concentration of NaCl increased. **b)** Similarly, the development rate increased with the strength of the applied positive electric potential.

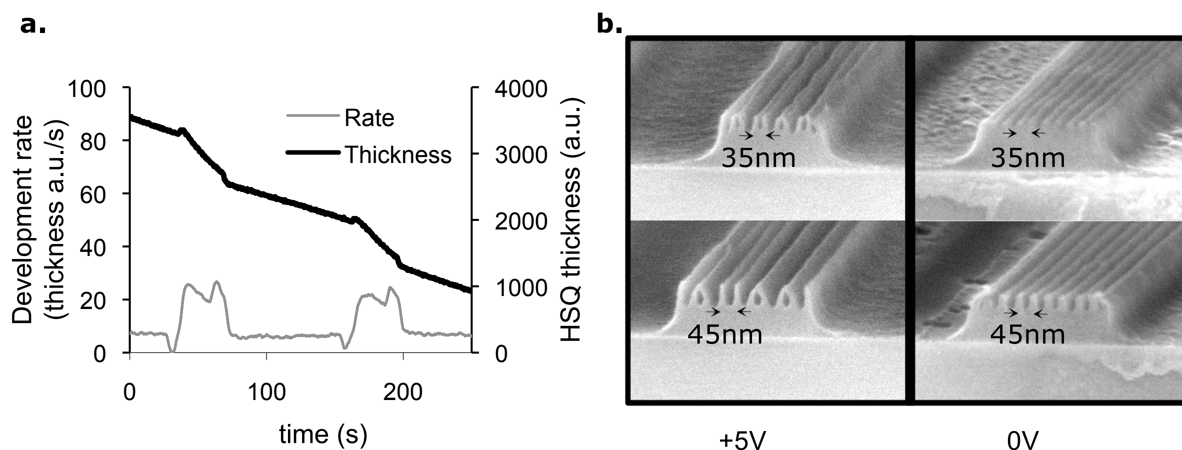

Figure 2.

a) A quartz crystal was coated with 96 nm of HSQ then placed in an O_2 plasma asher for 30 s at 150 W in order to partially crosslink the HSQ film. 1% NaOH developer solution was passed over the HSQ in a microfluidic module. A positive electric potential of 2.5 V was applied to a gold electrode beneath the HSQ from 35 s to 65 s causing a sharp increase in the development rate. At 160 s to 190 s, 4 V was applied to the crystal.

b) In these cross-section SEM images, approximately 175 nm of HSQ (Dow Corning 6 %) was spun onto a highly p-doped silicon substrate. A 500 μm long line pattern was exposed onto the samples using a Raith 150 lithography tool. These patterns were then developed in 1% sodium hydroxide developer solution for 45 s. An increase in resist removed between the features was evident when a positive 5 V potential was applied to the substrate surface.