

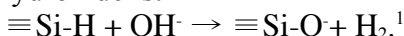
Electrochemical Development of Hydrogen Silsesquioxane

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Hydrogen silsesquioxane (HSQ) is an important resist for sub-10-nm electron-beam lithography. Densely packed nested-L test structures with a pitch as small as 9 nm have been fabricated using HSQ in a high-contrast salty developer solution.¹ However, the development mechanism for HSQ is still not well understood. A proposed chemical reaction to describe the development of HSQ in sodium hydroxide is:



The key result of this reaction is the conversion of HSQ into water-soluble, negatively charged ions. The regions of HSQ exposed by an electron beam are cross-linked and insoluble in aqueous solution.² It was suggested by some of us previously that a negative charge builds up on the surface of these cross-linked features during development, limiting HSQ removal between densely packed features.³

With the motivation of increased resolution for densely packed structures and improved understanding of the HSQ development mechanism, we present a study on the effect of electric potentials on development. The application of either a positive or negative potential of 2.5 – 10V to the substrate material resulted in increased development rate and improved resist clearing in between exposed structures (Fig 1). Remarkably, we also developed high-resolution HSQ features in a non-alkaline saltwater solution (4% NaCl in DI water) with the application of a negative potential (Fig 2). Furthermore, we developed HSQ in deionized water by applying a large potential.

To explain these observations, we hypothesize that when a positive potential was applied to the substrate material it offset the repulsive negative surface-charge, effectively shortening the Debye length and increasing the concentration of hydroxide ions close to the feature surface. Conversely, when a negative potential was applied, gas formed, suggesting the hydrolysis of water into H₂ and OH⁻. This localized formation of hydroxide ion could then explain the improvement in HSQ development. These results suggest that the development of HSQ is controllable by surface electrochemistry. By manipulating the electric potential of the substrate material during development, one can create high resolution features with a more defined shape.

1. J. Yang, B. Cord, K. Berggren, J. Klingfus, S. Nam, K. Kim, and M. Rooks, "Understanding of Hydrogen Silsesquioxane Electron Resist for Sub-5-nm-Half-Pitch Lithography." *J. Vac. Sci. Technol* vol. 27, n 6, p. 2622 – 2627, 2009

2. C. Allison, S. Kowarik, A. Schwartzberg, O. Nicolet, S. Lim, S. Leone, "Observing hydrogen silsesquioxane cross-linking with broadband CARS." *Journal of Raman Spectroscopy*, vol. 40, is. 7, p. 770 – 774, 2009.

3. B. Cord, J. Yang, H. Duan, D. Joy, J. Klingfus, K. Berggren, "Limiting Factors in Sub-10-nm Scanning-Electron-Beam Lithography." *J. Vac. Sci. Technol.*, vol 27, is. 6, 2009.

Figures:

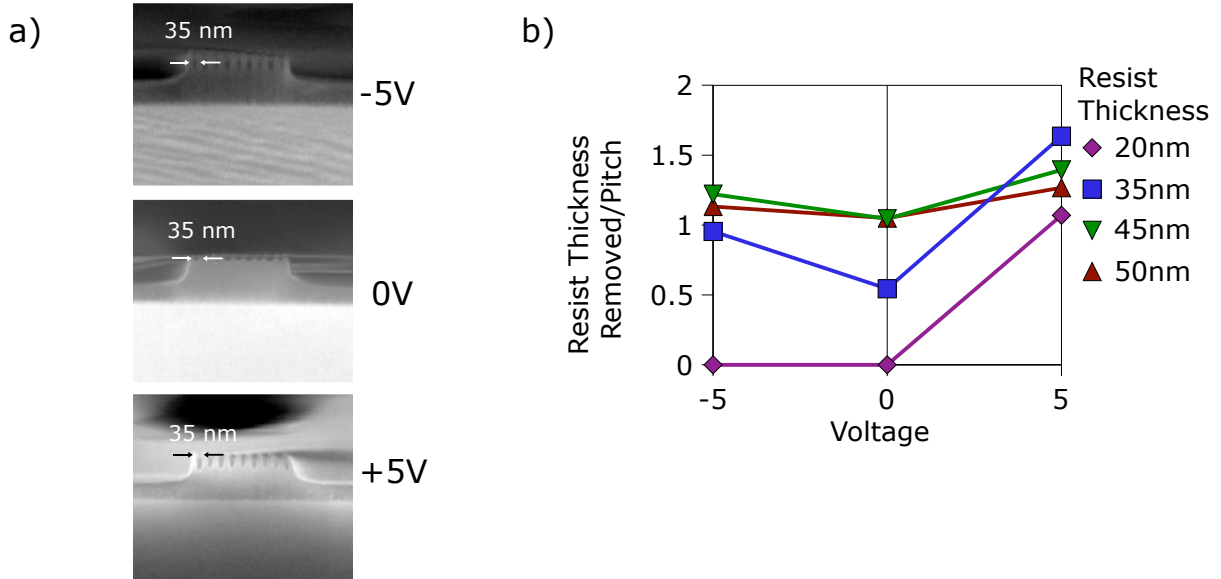


Figure 1. Electric potential with salty developer: a) The Raith 150 electron-beam lithography tool was used to take cross-section images of wafers developed with and without an applied potential. The improvement yielded by applying a potential is evident in these images of 180 nm thick resist with 35 nm pitch. b) The normalized resist thickness removed is the ratio of resist removed to pitch. Increasing this ratio indicates an improvement in the developer’s ability to remove more resist at smaller pitches. A positive 5V potential applied to the substrate surface during development yields the highest ratio.

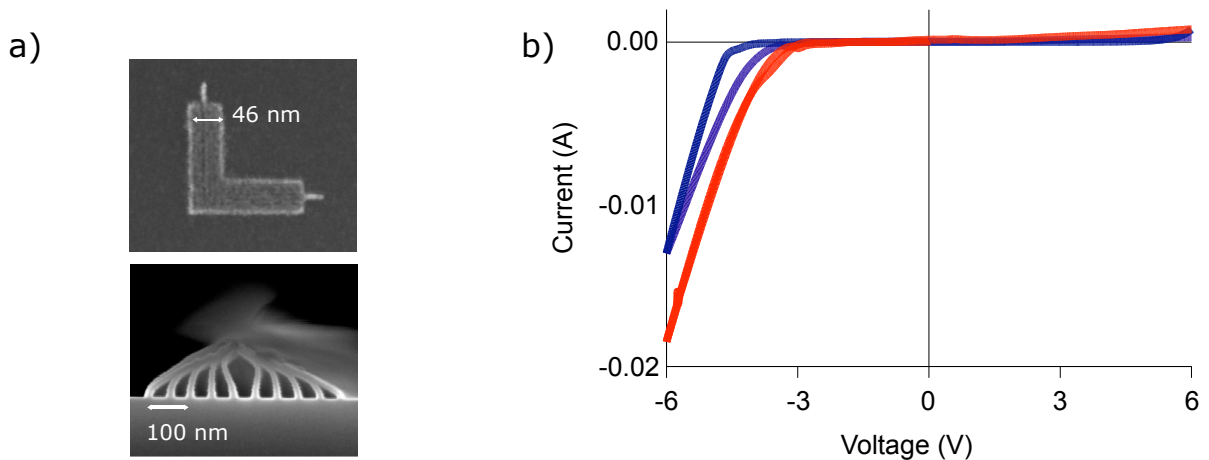


Figure 2. Electric potential in saltwater: a) High resolution features developed using an applied potential in 4% saltwater solution. The top image is a plain view of a nested-L test structure with 8 nm pitch. The bottom picture is a cross-section image of lines with 50 nm pitch. The structures fell over due to their high aspect ratio. b) The I-V curve for silicon with a platinum counter-electrode in saltwater. The red line shows the first cycle of applied voltage and the blue is the second cycle.