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### **Title**

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### **Author**

Griedel, Brian D.

### **Publication Date**

2009-07-20

## Understanding the mechanism of base development of hydrogen silsesquioxane

Jihoon Kim, Weilun Chao, Xiaogan Liang, Brian D. Griedel, and Deirdre L. Olynick

*Center for X-ray Optics, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720*

*Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720*

*Rigel, Inc., South San Francisco, CA, 94080*

*e-mail: JNKim@lbl.gov*

There have been numerous studies of electron beam exposed hydrogen silsesquioxane (HSQ) development conditions in order to improve the developer contrast. For TMAH based development, improvements were made by going to higher TMAH normalities and heating the developer.<sup>1,2</sup> Yang and Berggren showed development of electron beam exposed (HSQ) by NaOH with added Na salts (various anions) significantly improves the contrast.<sup>3</sup> Here, we study the contrast and etching rates of 100 keV exposed HSQ in NaOH in the presence of LiCl, NaCl, and KCl salts and use this as a segway to understand the mechanisms governing contrast during development HSQ development.

The basic mechanism of development of HSQ can be understood by comparing to etching of quartz in basic solutions.<sup>4</sup> Hydroxide ions act as nucleophiles which attack silicon. When a silicon-oxygen bond of the Si-O-Si matrix is broken, Si-O<sup>-</sup> and Si-OH are formed which can reversibly react to form the original structure. When a Si-H bond is broken via reaction with hydroxide, Si-O<sup>-</sup> and H<sub>2</sub> gas are formed. Salts can change the etching rates as a function of dose in a non-linear fashion to increase etch contrast.<sup>3</sup>

Figs. 1, 2, and 3 show contrast curves for HSQ developed in 0.25 N sodium hydroxide and with the addition of NaCl, LiCl and KCl salts at several concentrations. NaCl addition resulted in the highest contrast. Contrast improves with additional salt concentration while sensitivity decreases. Interestingly enough, addition of salt decreases the removal of material of NaOH alone at higher doses while increasing the rate at lower concentrations. Addition of LiCl salts improves contrast over NaOH alone. Furthermore, the sensitivity at all doses increases as the LiCl concentration increases, a salting out effect. Similar to NaCl salt behavior, the addition of KCl salts, improves contrast at the expense of sensitivity. However, unlike NaCl, even at very high doses, KCl addition increases removal rate of HSQ. We propose explanations for these results by considering the change of nucleophilic strength of the OH<sup>-</sup> as a function of cation size and concentration, the ability for salts to block the surface etching, competition between bond breakage and recombination, and the density of the HSQ as a function of dose. Furthermore, we will discuss evolution of contrast as a function of development time in the context of our models.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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<sup>1</sup> W. Henschel, Y. M. Georgiev, and H. Kurz, *J. Vac. Sci. Technol. B* **21** (5), 2018 (2003).

<sup>2</sup> M. Haffner, A. Haug, A. Heeren et al., *J. Vac. Sci. Technol. B* **25** (6), 2045 (2007).

<sup>3</sup> J. K. W. Yang and K. K. Berggren, *J. Vac. Sci. Technol. B* **25** (6), 2026 (2007).

<sup>4</sup> M. Deleuze, A. Goiffon, A. Ibanez et al., *J. Solid State Chem.* **118**, 254 (1995).

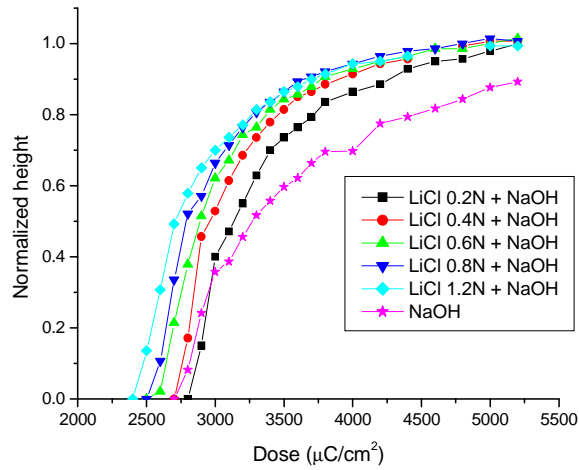


Figure 1. Contrast curves of HSQ development with sodium hydroxide solution, and sodium hydroxide solutions with various concentration of lithium chloride. The sodium hydroxide concentration maintains at 0.25N for all solutions. All developments were performed for 4 minutes at room temperature.

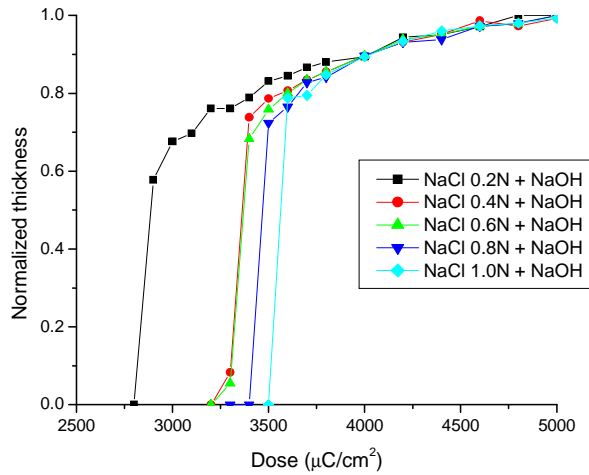


Figure 2. Contrast curves of HSQ development with 0.25N sodium hydroxide solutions with various concentration of sodium chloride. All developments were performed for 4 minutes at room temperature.

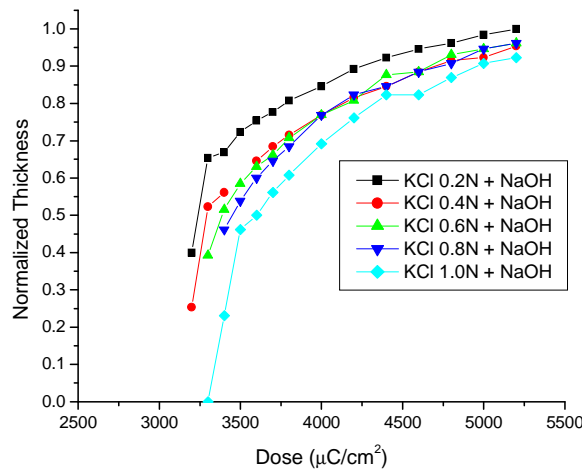


Figure 3. Contrast curves of HSQ development with 0.25N sodium hydroxide solutions with various concentration of potassium chloride. All developments were performed for 4 minutes at room temperature.