Using high-contrast salty development of hydrogen silsesquioxane for sub-10-nm half-pitch lithography

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When used as a negative-tone electron-beam resist, hydrogen silsesquioxane (HSQ) is typically developed in an aqueous alkali solution such as tetramethyl ammonium hydroxide. This development process results in low contrast. In this work, the authors instead used a mixture of salt and alkali to significantly increase the contrast of HSQ. Contrast values as high as 10 in a 115-nm-thick resist were achieved by developing HSQ in an aqueous mixture of NaOH alkali and NaCl salt. Remarkably, this salty developer resulted in contrast enhancement without significant decrease in resist sensitivity. The improved contrast of HSQ enabled the fabrication of 7 nm half-pitch nested-"L" structures in a 35-nm-thick resist with minimal loss in thickness using a 30 kV electron-beam acceleration voltage. They noticed a strong dependence of contrast enhancement on the concentration and type of cations and anions in the aqueous developer solution. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2801881]

I. INTRODUCTION

In electron-beam lithography (EBL), patterning resolution can be improved by (1) reducing the width of the electron-beam exposure point-spread function and (2) increasing the resist contrast. The minimum electron-beam point-spread function is constrained by the substrate and the type of EBL system used, which is not always easily modified. For instance, the smallest point-spread functions can be achieved by patterning on thin membrane substrates and using high electron-beam acceleration voltages. Using this method, Fischbein and Drndić[1] recently demonstrated fabrication of sub-10-nm structures using a 200 kV acceleration voltage electron-beam ablation of metals on a Si_3N_4 membrane. Fabrication of sub-10-nm isolated lines have also been demonstrated using electron-beam exposures in polymethyl metacrylate[2,3] (PMMA) and hydrogen silsesquioxane (HSQ).[4] HSQ is an attractive negative-tone electron resist that allows direct writing of etch-resistant silicon oxide nanostructures with low line-edge roughness.[5,6] However, the contrast of HSQ is poor, often resulting in undesired bridging or footing between closely spaced structures[7] and/or substantial loss in original resist thickness. Consequently, the fabrication of densely packed sub-20-nm pitch HSQ structures has not previously been achieved, even with extremely thin resist films (10 nm) and high electron-beam acceleration voltages (100 kV).[8] Recent efforts to increase the contrast of hydrogen silsesquioxane[6] have focused on developing with more concentrated alkalis[9] and elevating development temperatures.[10] These development methods showed improved contrast at the expense of reduced sensitivity. Furthermore, these strong developers can also cause material damage, and are thus unsuitable in certain situations: for instance, hot or concentrated alkalis will etch Si and hence are not compatible with Si substrate processing.

In this work, we instead increased the contrast of HSQ without reducing its sensitivity by adding salt (e.g., NaCl) to an alkali developer (e.g., NaOH). We came to this approach by first hypothesizing that the increased contrasts observed in Ref. 9 (from more concentrated developers) and Ref. 10 (from elevated development temperatures) were linked to increased reaction rates. Because studies on dissolution of phenolic polymers[11] have shown that the addition of salt to an alkaline developer will also increase reaction rates, and because the –OH functional group in phenolic polymers and –SiH functional group in HSQ are somewhat similar chemically, we hypothesized further that the addition of salt to an alkaline developer of HSQ may improve its contrast. The objective of this work was to test our hypotheses, to show the dependence of HSQ contrast on the concentration and types of salt, and to use this knowledge to fabricate high-resolution nanostructures.

We compared HSQ contrast curves for developments in different solutions and found that the best contrast of ∼10 in a 115-nm-thick resist was achieved by development in an aqueous mixture of 1 wt % NaOH and 4 wt % NaCl. This contrast value was a factor of three higher than what we measured for development in the conventional 25 wt % tetramethyl ammonium hydroxide (TMAH) developer. With this result, HSQ has been transformed from a low-contrast resist to one with contrast values approaching those of PMMA.

We also demonstrated that the resolution and fidelity of nanostructures fabricated by salty development is higher than the corresponding nanostructures developed in 1 wt % NaOH without salt. Using the salty developer, 14 nm pitch nested-"L" structures and 7 nm diameter nanodots on a
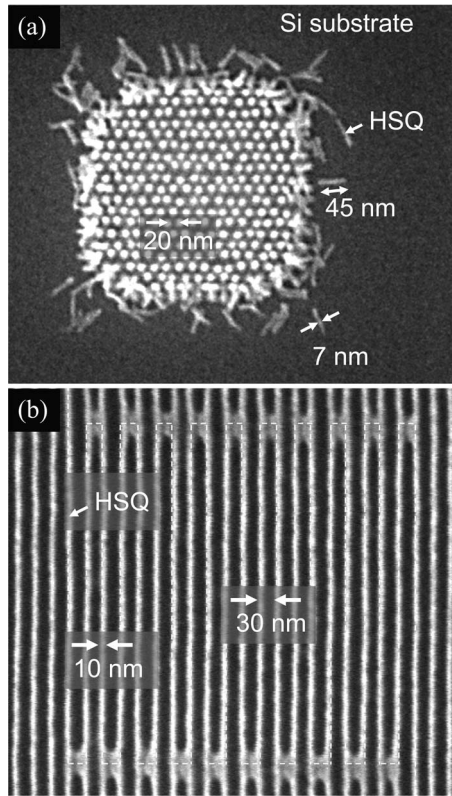
FIG. 1. SEM images of HSQ nanostructures on Si patterned at 30 kV acceleration voltage in a Raith 150 EBL system and developed using high-contrast aqueous 1 wt % NaOH and 4 wt % NaCl developer. (a) HSQ nanoposts with a center-center distance of 20 nm in a hexagonal close-packed structure in 45-nm-thick resist. The aspect ratio of the structures was ~6 as can be seen in the collapsed posts around the edges. (b) Boustrophedonic structure with 10-nm-wide lines on a 30 nm pitch exposed in 45-nm-thick HSQ. The dotted lines show the deliberately connected structure.

20 nm pitch in two dimensions could be resolved. Furthermore, isolated as well as dense lines were yielded with negligible loss in original resist thickness.

High-contrast and high-resolution patterning in HSQ has numerous potential applications. For instance, large-area patterning of dot structures, as shown in Fig. 1(a), might be used in the fabrication of high-density (~1.4 Tbit/in^2) bit-patterned media. On the other hand, the boustrophredonic structure featured in Fig. 1(b) might be used to make novel superconducting single-photon detectors.[12,13] Other potential applications of this salty development include higher-resolution photomask making and defining quantum dots for application to classical or quantum information processing. It may also be possible to use this development process on other resists with similar development chemistries.

II. EXPERIMENTS AND RESULTS

Contrast curves were obtained by the following procedure: we first spin coated 115 nm of HSQ (formulated as product XR-1541 6% solids from Dow Corning) onto a Si wafer. To avoid thermally induced contrast reduction, we did not bake the resist-coated wafer. A Raith 150 EBL system was used to expose a dose matrix of 10×80 μm^2 rectangles
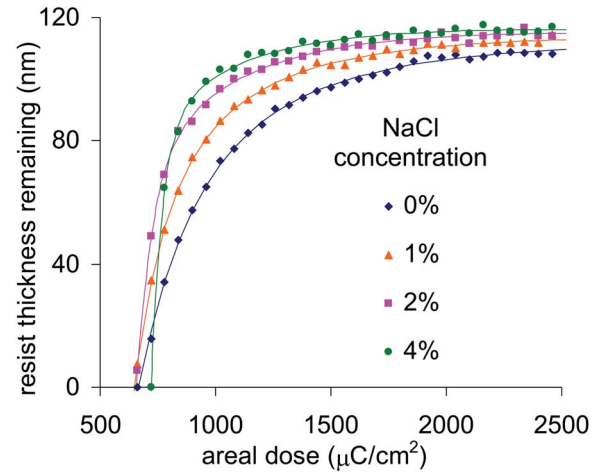

FIG. 2. Plot of remaining HSQ thickness vs area electron exposure dose for varying concentrations of NaCl in aqueous 1 wt % NaOH developer. Filled markers are data points while solid lines are fitting curves of exponential functions.

spanning a range of doses from 600 to 2500 μC/cm^2 at 30 kV acceleration voltage. Several sets of dose arrays were exposed in the same run on the same wafer to reduce variations between separate experimental runs. We then cleaved the Si wafer to separate out different dose-array sets and developed each set in different developer solutions. A pure alkali developer solution was first made, from which developer mixtures with different salt concentrations were derived. For instance, a pure alkali solution of 1 wt % NaOH was made by dissolving 5 g of solid NaOH pellets in 500 ml of de-ionized water. Then different amounts of NaCl salt were added to this original solution to get a constant alkali concentration for all developer solutions. Unless otherwise stated, developments were all carried out for 4 min at 24 °C to avoid temperature-dependent effects on the contrast. Finally, the thickness of each rectangle in the dose arrays was measured using a surface profilometer.

Contrast measurements for development in aqueous 1 wt % NaOH with varying amounts of NaCl salt is plotted in Fig. 2. We noticed that increasing the concentration of salt did not result in a significant increase in the onset dose (the maximum dose at which no resist remains), which in this case was ~650 μC/cm^2. Note also that the slope of the curves at the onset dose increased with increasing salt concentration, leading to the conclusion that the addition of salt to the developer increased resist contrast. In order to get a self-consistent measure of the contrast, we used a least-square error method to fit the data to the following analytical function:

$$\text{RTR} = \frac{T}{1+\eta}[(1 - e^{-(D-D_0)/A}) + \eta(1 - e^{-(D-D_0)/B})], \quad (1)$$

where RTR is the resist thickness remaining, T is the original resist thickness, D is the electron areal dose, D_0 is the areal dose at the onset of incomplete development, and A, B, and η are fitting parameters. This phenomenological expression was found to fit the data well over the entire dose range
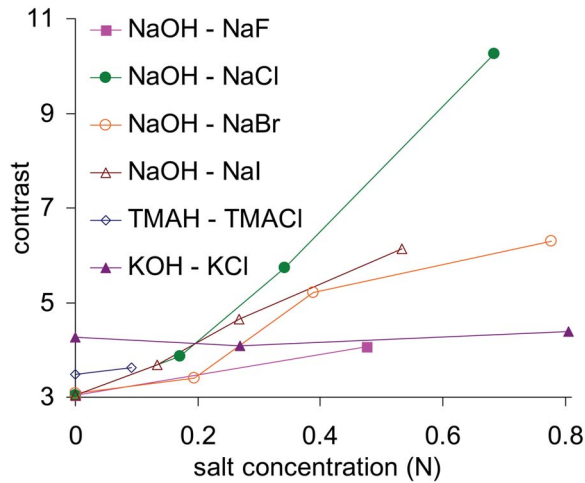
FIG. 3. Plot of contrast versus salt concentration expressed in normality (N). This plot shows the dependence of contrast enhancement on different cationic/anionic species. The highest contrast improvement was obtained for the NaOH–NaCl alkali-salt pair.
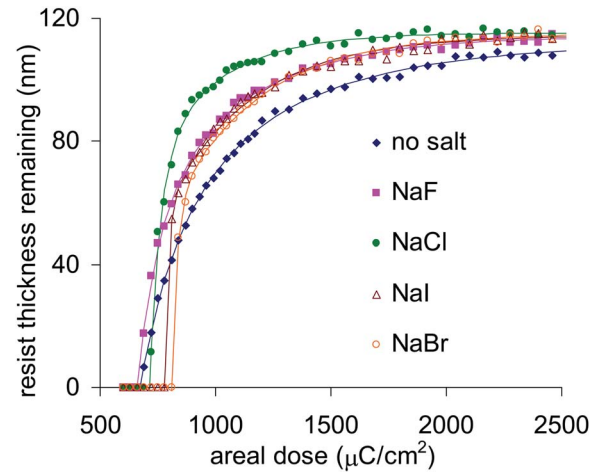

FIG. 4. Contrast curves corresponding to the highest measured contrasts for different sodium salts in 1 wt % NaOH. While similar curves were obtained for NaF, NaBr, and NaI above 700 μC/cm^2, the curve for NaCl was significantly different and had a much higher contrast value.

above D_0. We then extracted contrast values by finding the slope of a straight line connecting the point of zero resist thickness to the point of 75% of original resist thickness of the fitted curve on a semilog plot. In symbolic form, the contrast value was $0.75/\log_{10}(D_{0.75}/D_0)$, where $D_{0.75}$ was the areal dose at 75% of original resist thickness.

In addition to the NaOH–NaCl alkali-salt pair, we also investigated other alkali-salt pairs. This experiment studied the effect of different anions and cations on the contrast enhancement effect of salt. We always used alkali-salt pairs of the same cation to maintain the pH of the developer. The following alkali-salt pairs were studied: (1) NaOH–NaF, (2) NaOH–NaCl, (3) NaOH–NaBr, (4) NaOH–NaI, (5) KOH–KCl, and (6) TMAH-TMACl. For every alkali-salt combination, a set of contrast curves were obtained using the same procedure as discussed above. For these experiments, the concentration of KOH was 0.4 wt % (0.07N), concentration of NaOH was 1 wt % (0.25N), and concentration of TMAH was 2.38 wt % (0.26N).

Figure 3 is a plot of contrast versus concentration of salt expressed in terms of normality for a set of different alkali-salt pairs. Contrast enhancement with increasing salt concentration was observed for all alkali-salt pairs except for KOH–KCl. The alkali-salt pair consisting of NaOH–NaCl exhibited the highest contrast enhancement. Further, changing the anion from Cl to F, Br, and I exhibited a lower enhancement. The contrast values for NaOH–NaCl did not continue to increase beyond a salt concentration of ~4 wt %. Figure 4 is a plot of contrast curves corresponding to the best contrast values of Fig. 3 for development in 1 wt % NaOH with different sodium halides. Interestingly, the contrast curves for F, Br, and I anions lie almost on the same curve above 700 μC/cm^2 but that for Cl is significantly different. The data show that contrast enhancement is highly dependent on the type of cation and anion.

The contrast enhancement effect of NaCl in NaOH was also observed when we repeated the above experiments with

different development durations. Figure 5 is a plot of thickness remaining versus dose for two different development durations. In the case of development without salt, increasing the development duration from 2 to 10 min did not result in any change in the contrast curve. On the other hand, for development with salt, increasing the development duration further increased the contrast at the expense of a higher onset dose. This result suggested that the addition of salt resulted in contrast enhancement regardless of the length of development time.

Finally, we studied the effect of salty development on nanostructure fabrication. We tested the highest resolution we could achieve by exposing gratings and nested-"L" test patterns in a 45-nm-thick layer of HSQ on Si using a Raith 150 EBL system at 30 kV acceleration voltage, 120 pA beam current and single-pixel exposures for each line. The
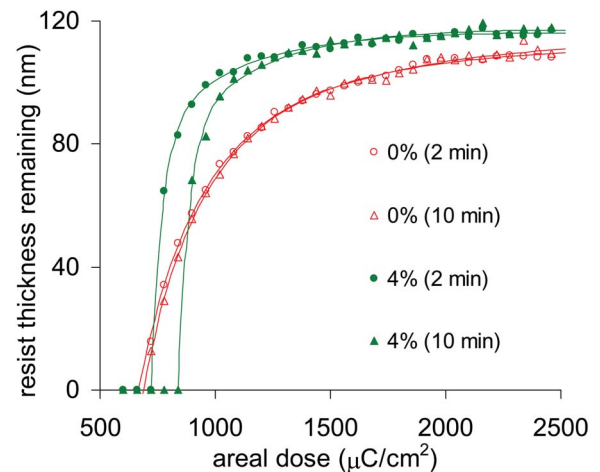

FIG. 5. Plots of thickness remaining vs exposure dose for development of HSQ in 1 wt % NaOH with two different salt concentrations and two different development times. A longer development time further improved the contrast for the salty developer, but did not affect the contrast when no salt was added.
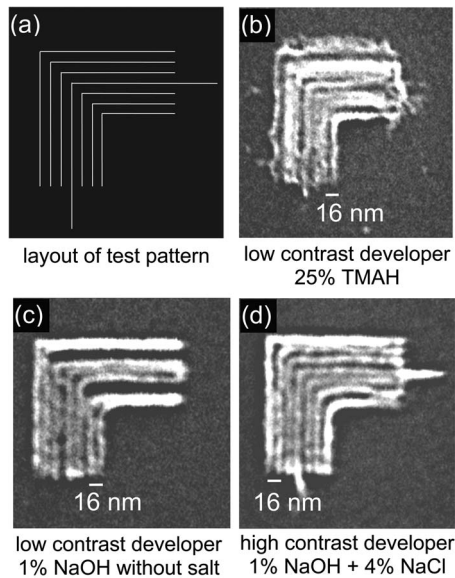
FIG. 6. 16 nm pitch nested-"L" structures. (a) Layout of dense and isolated lines forming the nested-"L" test structure. Exposure was done in 45-nm-thick HSQ at 30 kV acceleration voltage in a Raith 150 EBL system using single-pass line exposures of ~20 μC/cm dose for each line. Development was done in (b) 25 wt % TMAH, (c) 1 wt % NaOH without salt, and (d) 1 wt % NaOH with 4 wt % NaCl. Both dense and isolated lines yielded only in (d).
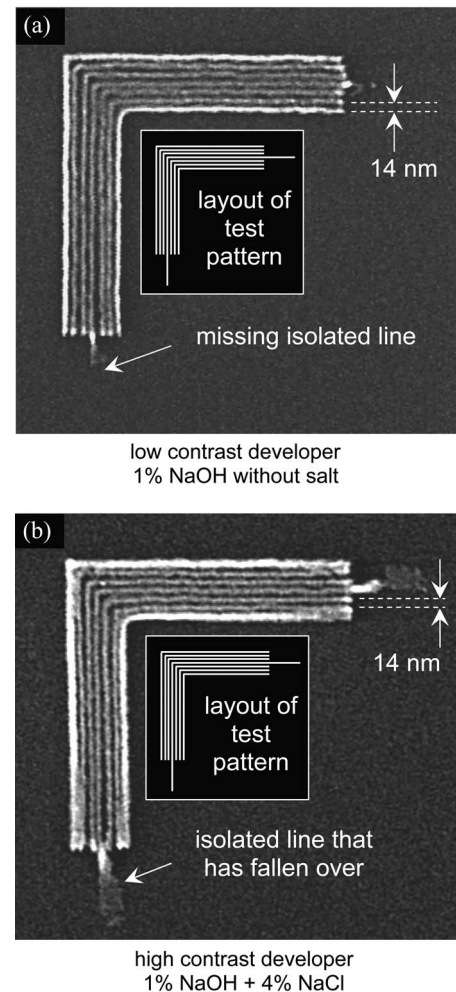

FIG. 7. SEM of 7 nm half-pitch nested-"L" structures exposed in 35-nm-thick HSQ. Development was done in (a) 1 wt % NaOH without salt and (b) 1 wt % NaOH with 4 wt % NaCl. Both dense and isolated lines yielded in (b) while isolated lines were missing in (a). The isolated line in (b) has fallen over. High-contrast development resulted in less loss in resist thickness than low-contrast development.

exposure line dose for these structures was ~1 nC/cm. The samples were developed in three different developers: (1) 25 wt % TMAH, (2) 1 wt % NaOH without salt, and (3) 1 wt % NaOH with 4 wt % NaCl. Developments were all done at 24 °C for 4 min. Figure 6 shows scanning-electron micrograph (SEM) images of 16 nm pitch nested-"L" structures developed using these three developers. Note that observing the difference in resolution between developers requires close attention. The nanostructures obtained from salty development were of higher fidelity than the corresponding structures developed in NaOH without salt or TMAH. For instance, the isolated line segments of the nested- "L" structures did not yield in Fig. 6(b) or 6(c) but yielded in Fig. 6(d). We observe that the resolution was much worse for development in TMAH. As shown in Fig. 6(b), the nested-"L" structures at 16 nm pitch developed in TMAH were not resolved at all.

In another experiment, we used a thinner resist film, this time 35 nm thick, and exposed nested-"L" structures with longer segments for the purpose of comparison between developments in 1 wt % NaOH with and without salt. As shown in Fig. 7, nested-"L" structures with a linewidth of 7 nm in a pitch of 14 nm could be resolved using both developers. The difference, however, was that the isolated line structure was again missing for low-contrast development, while both isolated and dense lines yielded for high-contrast development. The isolated line in Fig. 7(b) had collapsed on its side. Measurement of the width of this collapsed structure gave us its height (remaining resist thickness) of ~30 nm, which was close to the original resist thickness. Due to their higher aspect ratio, the structures in Fig. 7(b) tended to col-

lapse or stick together more readily than the corresponding structures in Fig. 7(a). We can conclude here that a high-contrast development does indirectly lead to higher resolution, as the resultant resist structures are thicker/taller and, therefore, are more suitable for subsequent pattern-transfer steps (e.g., by reactive-ion etching).

III. DISCUSSION

The high-contrast salty development process has enabled us to fabricate dense high-resolution structures with minimum loss in resist thickness. However, it should be possible to fabricate even higher-density structures by using a combination of different contrast enhancement techniques. For instance, we could use a combination of high-temperature, concentrated alkali and salty development to achieve the highest possible contrasts. Further improvement in resolution could also be attained by using thinner resist films and fabrication on thin membrane substrates.

The reason for contrast enhancement due to salt is unclear. The development mechanism of HSQ has been considered to consist of two main competing processes of dissolution and cross-linking.[14] We believe that the effect of the salt was to change the relative rates of dissolution and cross-linking by affecting the mean chemical activity of the ionic species present in the solution. For instance, a larger difference between dissolution and cross-linking rates can be seen as an explanation for increased contrast. An actual development mechanism might involve a complex interplay between chemical reactions and physical diffusion of reactants. While we do not provide a conclusive explanation at this point, these salty development effects could be a means to a better understanding of HSQ development mechanisms in future experiments.

IV. CONCLUSION

The central result of this paper is a new method to increase the contrast of HSQ by adding salt to an aqueous alkali developer. Contrast increased with increasing salt concentration while resist sensitivity did not change. The increased contrast of HSQ enabled high-resolution patterning of sub-10-nm structures. Using a Raith 150 EBL system at 30 kV acceleration voltage, we demonstrated the fabrication of 7 nm half-pitch nested-"L" structures where both dense and isolated-line structures yielded. Lower contrast development could not yield these structures at this resolution. We found that the contrast enhancement was sensitive to the type of anions and cations in the developer. The best contrasts were obtained using 1 wt % NaOH and 4 wt % NaCl.

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