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Understanding the Mechanism of Base Development of HSQ

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Abstract

We study the dissolution mechanism of HSQ (hydrogen silsesquioxane) in base solutions with the addition of chloride salts to elucidate the development mechanism. Reaction mechanisms are proposed based on the dissolution mechanism of quartz. Development kinetics points to two dose-dependent development mechanisms. Considering ion sizes, both hydrated and non-hydrated, and ion exchange, we propose that a combination of a surface dominated reaction at higher doses and a matrix dominated reaction at lower doses accounts for the high development contrast with a NaOH base/NaCl salt mixture. The interplay between the hydrated and non-hydrated ion size leads to higher contrast developers, such as tetramethyl ammonium hydroxide (TMAH) with NaCl.

Keywords: negative resists, dissolution mechanism, electron beam lithography, hydrogen silsesquioxane, HSQ, resist contrast, hydrated ion, non-hydrated ion.

I. Introduction

Significant effort has been taken to improve resist resolution for advanced

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nanoscience and technology. Features have been patterned below 10 nm for isolated lines. However, due to factors such as intrinsic electron scattering and resist properties, further shrinking of dimensions is limited. To minimize these problems, high accelerating voltage and thin resists have been introduced to minimize forward scattering whereas double patterning was developed to minimize proximity effects. Using a double patterning method, Weilun Chao *et al.*, demonstrated the fabrication of highly dense 15 nm Fresnel zone plates with polymethylmethacrylate (PMMA) on a Si_3N_4 membrane.[1] Improvements in resolution have often come about by manipulating resist process conditions such as the developer system. Yasin *et al.* achieved a feature size of 5 nm with high resist contrast by employing isopropyl alcohol (IPA) and water instead of using conventional methyl isobutyl ketone (MIBK) and IPA developers.[2] Cold developers were also discovered with PMMA to yield high resist contrast .[3]

Hydrogen silsesquioxane (HSQ) is a highly attractive negative tone resist due to its relatively high resolution, low line edge roughness, high etching resistance and high mechanical strength. With a thin HSQ layer (~ 10 nm), sub-20 nm pitch HSQ structures have been reported,[4] and in the bilayer combination, HSQ can give a high aspect ratio exceeding 15.[5] Problems with HSQ have been reported, including instabilities in the resin and exposure dose that is dependent on the area exposed (unrelated to electron scattering effect)[6,7] These issues can be mitigated with strong developers but at the expense of sensitivity.[8]

Since the use of HSQ as a resist was initially reported,[9] numerous efforts have been made to increase the resolution/contrast of HSQ. For TMAH-based development, improvements in resist contrast were made by going to higher TMAH concentration and higher development temperature.[8,10] Recently, Yang and Berggren showed that the addition of salts into NaOH base solution for developing electron beam exposed HSQ can significantly improve the contrast without reducing the sensitivity compared to development in NaOH

alone.[11] High resolution was demonstrated, 7 nm half pitch patterns in approximately 30 nm thick HSQ. However, the mechanism for achieving such high contrast was not explained.

In this work, we investigate the development and contrast of HSQ in NaOH solutions with varying concentrations of salts in order to understand the development mechanism in aqueous base and explore the possibility resolution and sensitivity improvements. High contrast mechanisms are proposed considering important contributing factors such as ion mobility, ionic size, electrostatic interaction, cationic exchange and hydroxide ion. To come to the mechanism of high contrast with salt, several experiments had to be conducted. First we investigated HSQ development contrast in NaOH with the addition of three salts: LiCl, NaCl, and KCl. To understand the role of cation electronegativity and the ability to dissociate and interact with the HSQ during development, we looked at ion exchange between Na ions and cations of three salts, LiCl, KCl, and tetramethyl ammonium chloride (TMACl) using the contrast measurements. To further understand dissolution mechanisms, we compared kinetics of the development using NaOH with the addition of either NaCl or KCl. From all this data, we were able to propose two mechanistic pathways for development. This is used to understand contrast and sensitivity changes of NaOH with varying salt concentrations (3 salts: LiCl, NaCl, and KCl). Finally, with the understanding of how high contrast presents, we test a new developer and are able to achieve improved contrast and sensitivity.

II. Proposed development mechanism of HSQ

Although there are numerous studies of HSQ development, there are few discussions of the development mechanism. Namatsu *et al.* suggested that the dissolution of HSQ in base developer is probably associated with ionization by bond scission.[9] Schmid *et al.* alluded to a competition between etching and recombination in base.[12]

In Figures 1a and 1b, we present the role hydroxide ions play in the dissolution of

HSQ. Nucleophilic hydroxide ions (e.g. using sodium hydroxide) attack electropositive silicon atom. When a Si-H bond is broken via a reaction with hydroxide, Si-OH and H_2 gas are formed via the dehydrogenation reaction (Fig. 1a) wherein hydride ion deprotonates e.g. a water molecule in the solution (the hydride could also abstract a proton directly from the SiOH just formed). The deprotonation of water forms another hydroxide which can coordinate with the sodium ion. This hydroxide can then deprotonate the Si-OH to form another water molecule and the sodium silicon oxide. Because silicon-hydrogen bonds (~310kJ/mole) are weaker than silicon-oxygen bonds (~464kJ/mole), the breaking of the Si-H bond over the Si-O bond is favored.[13,14] This reaction is consistent with the results obtained by T. C. Chang *et al.*, in which the Si-H peak in HSQ disappears in FT-IR spectra after treatment with a strong alkaline solution.[15] After dehydrogenation, HSQ can be solvated by aqueous base. Dissolution will be higher when there are more solvation sites or when the molecular weight is lower.

The importance of solvation has been demonstrated in organic solvent development of HSQ.[12] Unexposed material was found to dissolve in a variety of solvents including MIBK and xylenes. As these developers are only able to solvate the material, whole chains of HSQ are removed. However, the resolution was much lower than in aqueous base development, indicating that aqueous base can remove the material that is cross-linked during exposure (higher molecular weight). This is due in part to the breaking of Si-O bonds in aqueous base which reduces the molecular weight of HSQ chains, enhancing dissolution. When a silicon-oxygen bond is broken, $Si\text{-}O^-$ and Si-OH are formed. This can either reversibly react to form the original structure or be solvated and contribute to the dissolution of the material. (Schmid et al. [12] may have been alluding to this when he discussed the competition between etching and recombination). Stress in the bonds and high alkalinity can drive the process towards dissolution.

In addition, the addition of salts can enhance dissolution. Similar to what happens in quartz (Fig. 1b),[16] cations from the salt coordinate with the lone electron pair on the oxygen, acting as Lewis acids, which increases the activity of the silicon reaction site and weakens the Si-O bond - further enhancing HSQ dissolution. This mechanism explains how dissolution can be faster in the presence of salt cations, but does not explain the nature of high contrast which is a dose dependent dissolution. These mechanistic aspects are discussed herein.

III. Experiments

HSQ was obtained from Dow Corning as a 6% solution in MIBK and spin-coated on prime silicon wafers at various speeds from 1500 to 2000 rpm for 45 sec to achieve nominally 160 nm films. Then, the wafer was vacuum dried at 26°C for 5 min. Exposures were performed on either a Leica VB6HR tool or a Vistec VB300 operating at 100 keV with a beam current in the range of 400-500 pA. The films were developed immediately after exposure at room temperature by immersion.

Appropriate concentrations of base developers were prepared with a volumetric flask with the following reagents in deionized water: NaOH (VWR International); 25 wt. % TMAH in water (Alfa Aesar); KOH (Alfa Aesar); LiOH (Sigma-Aldrich); NaCl (EMD Chemicals Inc.); KCl (VWR International); LiCl (Mallinckrodt Chemicals) and TMACl (J. T. Baker). Developers were used approximately 36 hrs after being prepared.

After development, wafers were rinsed in deionized water for 10 sec to remove residual developers. Thickness measurements for contrast curves were obtained using Alpha-Step 500 surface profiler (Tencor Instrument) or a Digital Instruments atomic force microscope (AFM) depending on the size of the pattern exposed. Feature sizes varied between experiments and are mentioned in the subsequent text. Note, although the contrast trends with salt and dose were the same when different feature sizes were developed, the

absolute contrast was a function with feature size, consistent with an area dependent dose.[6,7]

IV. Development in NaOH with the addition of LiCl, NaCl and KCl

Based on the proposed mechanism, the activation of the silicon-oxygen reaction site activity as a function of the additive cations changes the dissolution rate. Cations can act as Lewis acids, coordinating with oxygen lone pair electrons and facilitating Si-O bond cleavage, thereby enhancing dissolution of HSQ. Lewis acidity decreases in the following order: Li > Na > K. From this trend, we would assume that dissolution rate of HSQ will increase in the order of salt additions: LiCl > NaCl > KCl. Figure 2 compares HSQ contrast curves using four developers: NaOH 0.25N alone and NaOH with the addition of 0.2 N LiCl, NaCl, or KCl. The feature size exposed was 10x80 μm and the development was 4 minutes at room temperature. Contrary to our assumption, LiCl addition, under these conditions, creates the least aggressive developer with the lowest gel dose and relatively high remaining thickness in the high dose region. Additions of KCl created the most aggressive developer in the high dose region (least remaining thickness). With NaCl additions, the highest contrast was achieved as it was least aggressive in the high dose region (highest remaining thickness) and most aggressive in the low dose region (highest onset dose). The behavior of lithium suggests its more covalent bonding nature to its counter ion retards lithium's role as a strong Lewis acid acting on oxygens of the matrix. Thus we studied the role of counter ion dissociation.

V. Ion exchange in base/salt solutions

To study counter ion dissociation, we looked at potential ion change in the developer solutions. For these experiments we compared Na ion exchange with three cations: Li^+, tetramethyl ammonium (TMA^+), and K^+ ions in base/salt mixtures. Contrast was measured with four solutions for each of the three exchange tests:

1) 0.25 N NaOH + 0.25 N XCl (X = Li, TMA, or K)

2) 0.25 N XOH + 0.25 NaCl

3) 0.25 N NaOH

4) 0.25 N XOH

If the exchange goes to equilibrium, solutions 1 and 2 should give the same contrast curves. Solutions 3 and 4 are reference standards. The four solutions were allowed to sit for approximately 36 hours before being used.

Results show that the amount of ion exchange depends on the cation combinations (Fig. 3). Lithium ion, Li^+, is very tightly bound to its anion (Fig. 3a), such that substitution of Na^+ in NaOH with Li^+ in LiCl rarely happens (solutions 1 and 2 behave very differently). Furthermore, LiOH is a much weaker developer than NaOH (due to less availability of OH^- presumably due to more covalent nature of lithium's bond to the OH^-), and LiCl addition to NaOH does nothing to increase the dissolution over NaOH alone (little Li^+ coordination with the lone pair oxygen in the Si-O bond).

Contrary to Li^+ in LiOH or LiCl, TMA^+ ion with the Na+ ion appear to exchange such that development in solutions 1 and 2 yields very similar contrast curves. In addition, note that TMAH is a less aggressive developer (more sensitive, lower onset dose) than NaOH. We believe this is related to the larger ionic radius of TMA^+ which will be discussed in more detail in a subsequent section.

For the exchange of Na^+ and K^+ ions, the behavior is quite complex. The exchange does not reach an equilibrium as reflected in the different HSQ development contrast with solutions 1 and 2. Furthermore, similar to the addition of NaCl to NaOH, the addition of NaCl to KOH increases contrast. Moreover, NaOH and KOH developers behave similarly without salt addition. To understand the role of NaCl salts in increasing the contrast, we investigated the dissolution kinetics more directly.

VI. Development Kinetics

To better understand the development behavior of HSQ, we investigated the kinetic behavior for the development. Features 1x1μm were exposed as a function of dose at 100keV (features are smaller to reduce electron beam writing time) and developed in either NaOH 0.25N/NaCl 0.8N or NaOH 0.25N/KCl 0.8N for various times. Contrast graphs were produced using AFM measurements. Figure 4 shows dissolution rates (slopes of thickness-vs.-time curves, Fig. 4a) at selected doses and resulting contrast curves for two development times (Fig. 4b). At the lower dose (3400μC/cm^2), dissolution rate is faster and appears linear for both developers. At the higher doses (4000 μC/cm^2 & 4900μC/cm^2) with the KCl developer, the material begins to dissolve and then stops. With NaCl, the etching is overall more aggressive than KCl at the middle dose (4000 μC/cm^2). The etching starts at a slower rate, stops, and then starts again at a much higher rate. At the highest dose (4900 μC/cm^2) NaCl shows similar behavior to that with KCl, that is, initially dissolving and then stopping. However, the dissolution is slower at the same dose in NaCl compared to KCl. This overall behavior results in higher contrast for NaCl over KCl additions to NaOH. The dose dependent etch rate behaviors as seen in Fig. 4 suggest that there are multiple etch mechanisms at play. In the next section, we propose two dissolution mechanisms.

VII. Dose Dependent Development Mechanism

To understand the development mechanisms, we consider factors such as ion mobility, ion size, electrostatic interaction, cationic exchange and relative reactivity of hydroxide ions (for example, based on counter ion). Two dissolution mechanisms are proposed 1) surface dominated reactions and 2) matrix dominated reactions. The synergy of these two mechanisms, and the role of cation size in the hydrated and non-hydrated form, results in higher contrast with the addition of NaCl salts.

After the dehydrogenation reaction with OH^-, the HSQ surface will be negatively charged, attracting salt cations to the surface (Fig. 1a). This can produce an electrostatic double layer which impedes hydroxide ion diffusion to the surface.[17] The salt cations passivating the surface will be in solution and thus transport of the hydroxide to the surface through this double layer will depend on the *hydrated* cation size. Table 1 shows hydrated and non-hydrated cation sizes for the ions studied here. Although K^+ ion is larger than Na^+, K^+ has a smaller hydrated size. At lower doses, dissolution is faster because the HSQ has lower molecular weight, so we suspect that the formation of the electrostatic double layer plays a smaller role; it takes less ionization events (Fig. 1a and 1b) to solvate and dissolve HSQ chains. At higher doses, more ionization events are required to solvate and dissolve the materials, if it can be dissolved at all. So, as dose increases the electrostatic double layer becomes greater in extent. The penetration of the hydroxide ions and the activating cation in the salt is thus more affected by the electrostatic double layer and penetration through a potassium electrostatic double layer is easier than through a sodium electrostatic double layer. Hence, NaOH/KCl is more aggressive than NaOH/NaCl at the highest doses (Fig. 4), with potassium's smaller hydrated radius. Another factor to consider, is ion mobility.[19] In aqueous solution, hydrated potassium ion has a higher mobility than hydrated sodium ion and will facilitate higher K^+ concentrations at the surface.

The second important mechanism is related to diffusion of the salt cation into the matrix. In the matrix or near the surface, where space is more constrained, non-hydrated ion interaction is dominant. Sodium can penetrate into the matrix faster than potassium because of its smaller *non-hydrated* ionic radius (Table 1). Also, sodium has higher electrostatic interaction with oxygen in HSQ due to its higher electronegativity compared with potassium. Hence, NaCl additions will lead to a more aggressive developer when the matrix reaction dominates (high rate for NaCl at 4000 $\mu C/cm^2$, Fig. 4). However, at very high doses, the

matrix is denser,[6] so ion penetration into the matrix is limited. Consequently, we believe surface etching is dominant, similar to the etching of quartz. When surface etching dominates, addition of KCl makes the more aggressive developer (higher initial etch rate at 4900 μC/cm2, Fig. 4) for the reasons previously discussed (smaller hydrated radius of K^+).

Based on these two mechanistic pathways, we propose that high resist contrast of HSQ in NaOH with NaCl results from the combination of large hydrated ion size and small non-hydrated ion size. The larger hydrated ion size impedes surface etching which is the dominant mechanism at the higher doses. The smaller non-hydrated ion size and larger electronegativity of Na^+ speeds etching at intermediate doses over K^+.

The contrast with the addition of LiCl is limited by the binding nature of Li^+ with the counter anion. Li^+ is tightly bound to its counter anion (demonstrated by the exchange reaction), and thus is less available to bind with an oxygen lone pair, leading to slower dissolution. Further, hydrated lithium ions are good at blocking OH^- penetration at the surface because of their larger hydrated radius. Hence additions of LiCl to NaOH reduces the etch rate over NaOH alone.

We have also studied contrast as a function of salt concentration of LiCl, NaCl, and KCl in NaOH. As the salt concentration of LiCl increases, etching is reduced most likely due to LiCl build-up at the surface which impedes the etching. Additions of NaCl increase the onset dose potentially because the higher concentration increases the diffusion into the matrix and enhances the dissolution rate. Higher concentrations of KCl increases the overall development rate at all doses. However, understanding the competition between surface dominated reaction, cations building up at the surface and impeding the resist dissolution, and matrix dominated reaction would be facilitated by dissolution rate measurements as a function of salt concentration and is a topic for future study. Another open question is why the etching at high doses starts but then stops (at least over the time frames we studied, Fig. 4,

4000 μC/cm2, Fig. 4). We suspect this is related to the charge density at the surface from the electrostatic double layer, but this needs further investigation.

Based on the proposed mechanistic pathways, we investigated the interplay between a large hydrated radius and a small non hydrated radius. Out of the ions studied, we chose TMA^+ because it has a large hydrated radius and good dissociation (with lower electronegativity relative to Li^+, Na^+ and K^+). A developer solution of TMAH 0.25N with NaCl 0.8N (4 min. development time) was compared with NaOH 0.25N with NaCl 0.8N (4 min. development time). Results in Figure 5 show that TMAH with NaCl has slightly higher sensitivity and higher contrast compared with NaOH with NaCl. As we observed in ion exchange experiments, TMA^+ and Na^+ ions have almost complete exchange. Therefore, the actual composition of 0.25N TMAH/0.8 N NaCl solution should be TMAH, NaOH, and TMACl, and a larger amount of NaCl. In this case, the smaller concentration of a larger hydrated ion, TMA^+, more effectively blocks cations and OH^- at the surface in the high dose region. In addition, the Na^+ ion, with its smaller non-hydrated radius, can penetrate the matrix at the lower doses, making the tested mixture a more aggressive developer in the low dose region. As a result, the combination of these two factors, larger hydrated radius of TMA^+ and smaller non-hydrated radius of Na^+ acting in different dose regimes gives slightly higher sensitivity and resist contrast compared with NaOH/NaCl developer at the same salt concentration.

VIII. Conclusion

An HSQ development mechanism is proposed where salt cations interact as Lewis acids with oxygen in siloxane and thereby weaken the Si-O bond, facilitating attack of OH^- on silicon and dissolution of HSQ. Surface and matrix reaction mechanisms are influenced by factors such as ion size, electrostatic interaction, ion mobility, and reactivity of OH^-; these factors contribute to these dose dependent mechanisms. Electronegativity of the ions, ion dissociation, and hydrated and non-hydrated ion sizes are particularly important for the systems studied.

Based on dissolution rate measurements, we proposed two different dissolution mechanisms—a surface dominated mechanism and a matrix dominated mechanism. Hydrated ion size determines the concentration of ions that penetrate the electrostatic double layer and affects the etching rates. At high doses, the surface mechanism predominates and the salt cation with the smaller hydrated ion radius (K^+) results in the more aggressive developer. When ions can penetrate the matrix, the salt cation with the smaller non-hydrated radius gives the more aggressive developer. However, this depends on the amount of ion dissociation. Lithium was found to have the poorest dissociation of the ions studied. We also found the highest contrast HSQ developer by combination of TMA^+ and Na^+ ions in TMAH with NaCl solution (as compared with NaOH with NaCl) by taking advantage of the interplay between the two mechanisms.

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Fig 1. a) Proposed mechanism for H_2 evolution. b) Proposed dissolution mechanism of HSQ in base with salts. M^+ is salt cation.

Fig. 2. Comparison of NaOH 0.25N and three NaOH 0.25N with salt 0.2N developers. Salts = KCl, LiCl, or NaCl. All developments were performed for 4 minutes at room temperature. The three development data from NaOH 0.25N were averaged.

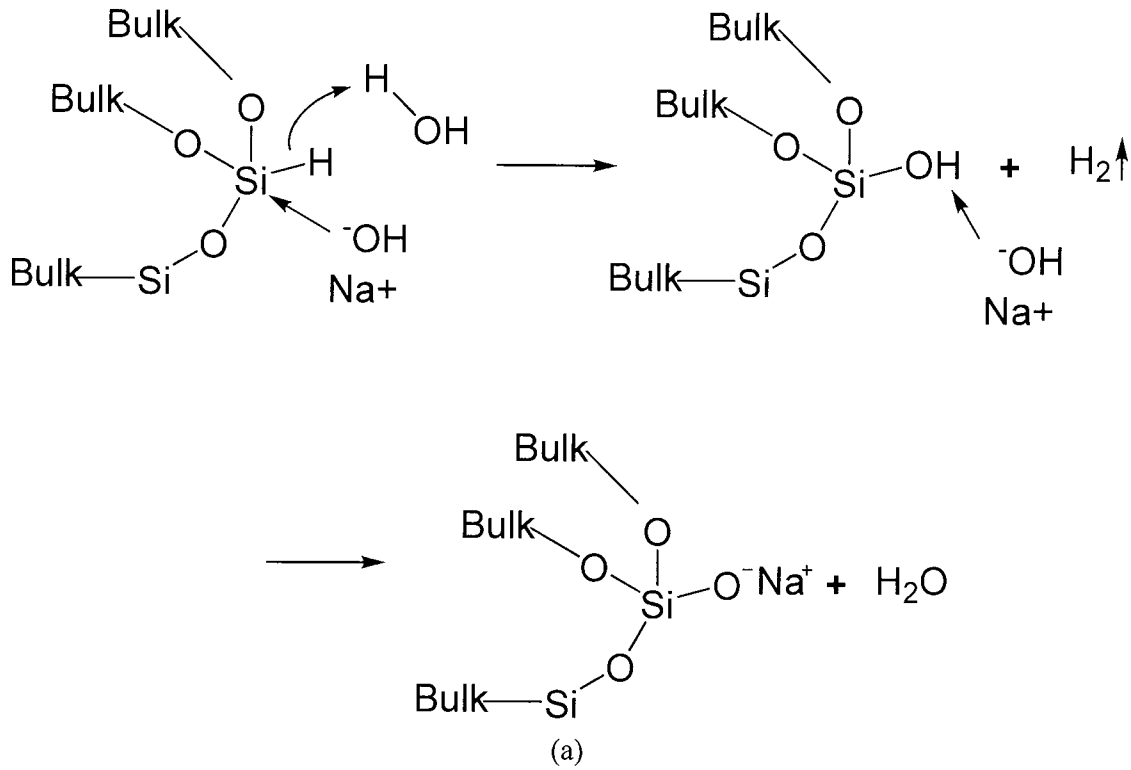
Fig. 3. Contrast curves of HSQ development in a) sodium hydroxide with lithium chloride and lithium hydroxide with sodium chloride, b) sodium hydroxide with tetramethyl ammonium chloride (TMACl) and TMAH with sodium chloride and c) sodium hydroxide with potassium hydroxide and potassium hydroxide with sodium chloride. All developments were performed for 4 min at room temperature. The hydroxide developer of the appropriate cation without salt is shown as a reference.

Fig. 4. a) Thickness change of HSQ as a function of time after being developed in NaOH 0.25N with NaCl 0.8N and with KCl 0.8N at room temperature, and b) contrast curves from this data at 20 and 30 seconds.

Fig. 5. Contrast curves of HSQ development in sodium hydroxide solution, and sodium hydroxide solutions with various concentration of a) lithium chloride b) sodium chloride and c) potassium chloride. The sodium hydroxide concentration was maintained at 0.25N for all solutions. All developments were performed for 4 minutes at room temperature. The three development data from NaOH 0.25N were averaged to compare graphs.

Fig. 6. The contrast curve from TMAH with NaCl is compared with that from NaOH with NaCl. 30x50 μm square patterns are exposed at 100keV and developed for a) 4 min and b) 8 min at room temperature. The contrast curves developed in hydroxide developer for 4 min are shown as reference in both graphs.

Table 1. Non-hydrated and hydrated size of ions[18]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OH
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H2
O
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Si
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+
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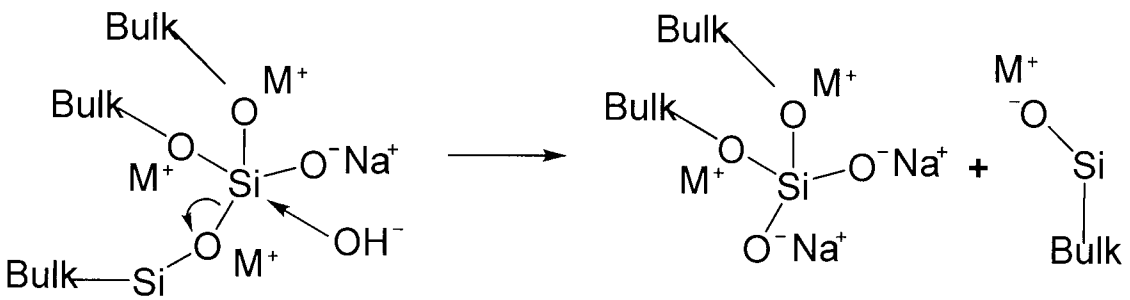
O
Bulk
Si

(a)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Bulk
O
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M+
Si
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O
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Bulk
Si
Bulk
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O
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+
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-O
Si
O-Na+
Bulk

(b)

Fig. 1

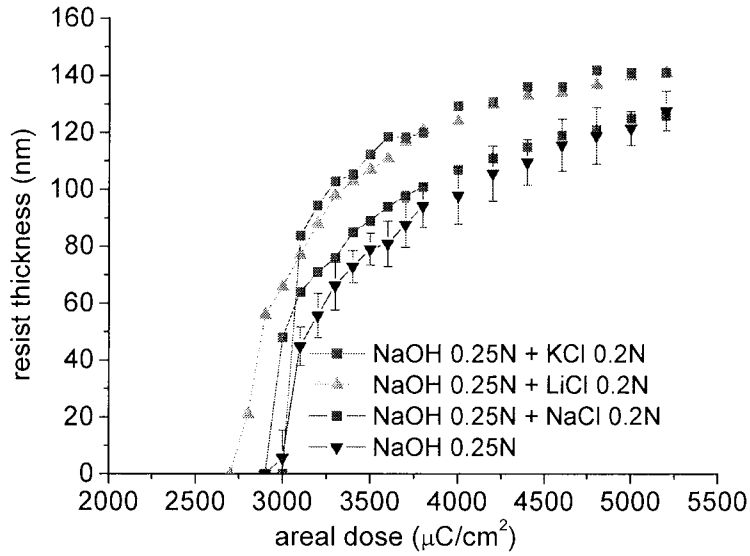
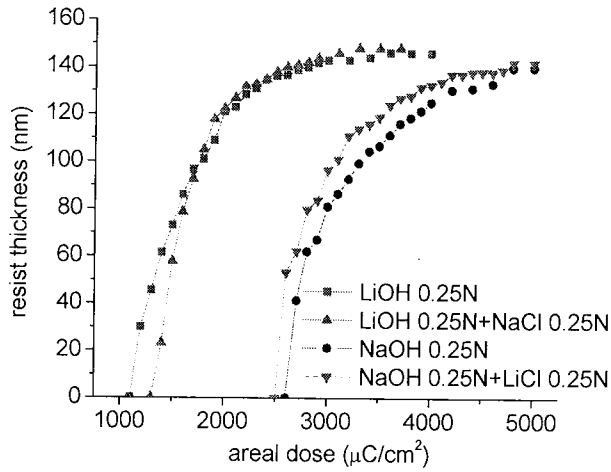

160
140
120
100
80
60
40
20
0
resist thickness (nm)
2000
2500
3000
3500
4000
4500
5000
5500
areal dose (μC/cm²)
NaOH 0.25N + KCl 0.2N
NaOH 0.25N + LiCl 0.2N
NaOH 0.25N + NaCl 0.2N
NaOH 0.25N

Fig. 2


resist thickness (nm)
areal dose (μC/cm²)
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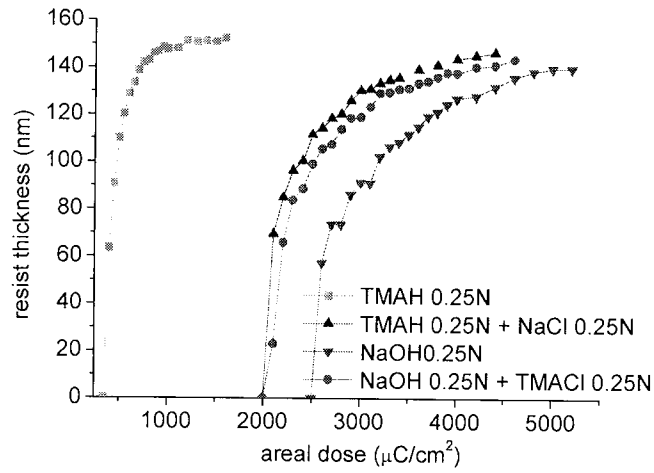
LiOH 0.25N+NaCl 0.25N
NaOH 0.25N
NaOH 0.25N+LiCl 0.25N

a)


resist thickness (nm)
areal dose (μC/cm²)
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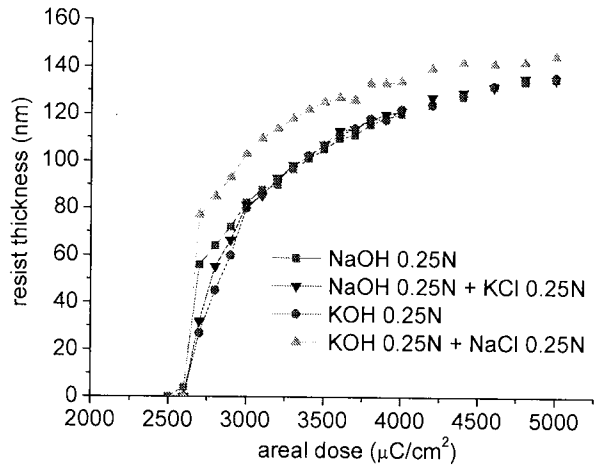
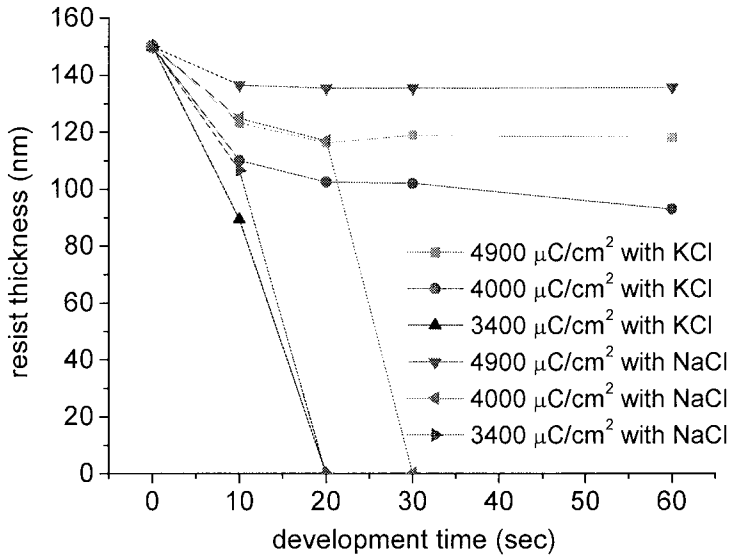
TMAH 0.25N + NaCl 0.25N
NaOH0.25N
NaOH 0.25N + TMACl 0.25N

b)

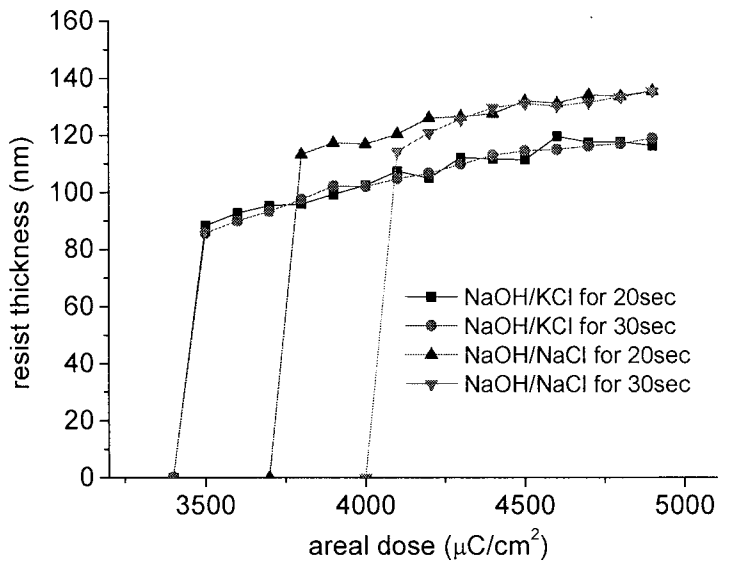

resist thickness (nm)
areal dose (μC/cm²)
NaOH 0.25N
NaOH 0.25N + KCl 0.25N
KOH 0.25N
KOH 0.25N + NaCl 0.25N

c)

Fig. 3


resist thickness (nm)
development time (sec)
4900 μC/cm2 with KCl
4000 μC/cm2 with KCl
3400 μC/cm2 with KCl
4900 μC/cm2 with NaCl
4000 μC/cm2 with NaCl
3400 μC/cm2 with NaCl

a)

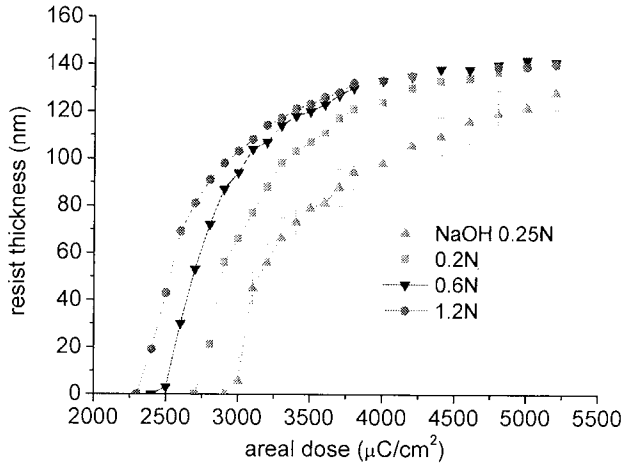

resist thickness (nm)
areal dose (μC/cm2)
NaOH/KCl for 20sec
NaOH/KCl for 30sec
NaOH/NaCl for 20sec
NaOH/NaCl for 30sec

b)

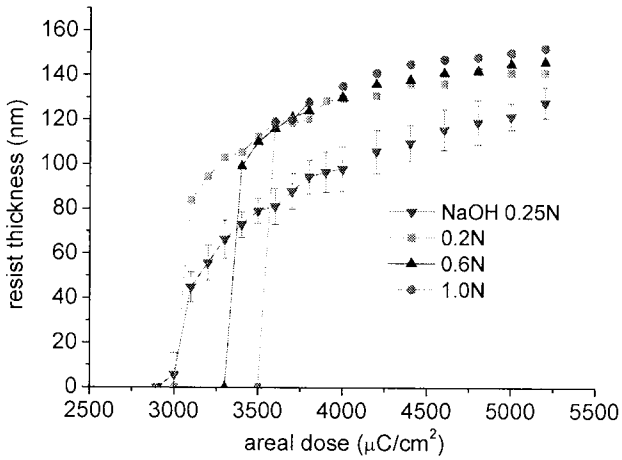
Fig. 4

Ion	TMA^+	Li^+	Na^+	K^+	Cl^-	OH^-
Non-hydrated radius (Å)	3.47	0.68	0.95	1.33	1.81	-
Hydrated radius (Å)	3.67	3.82	3.58	3.31	3.32	3.00

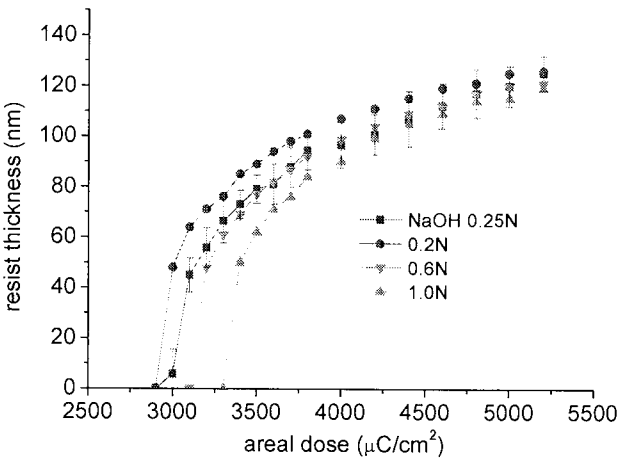
Table 1


resist thickness (nm)
areal dose (μC/cm²)
NaOH 0.25N
0.2N
0.6N
1.2N

a)

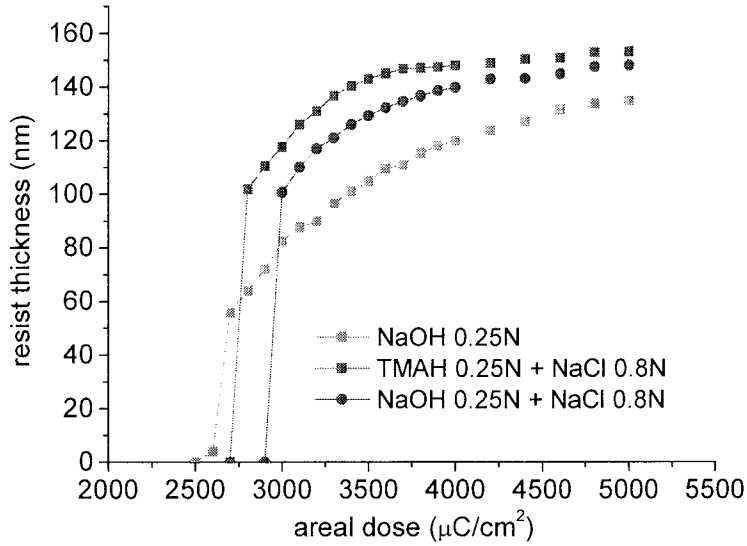

resist thickness (nm)
areal dose (μC/cm²)
NaOH 0.25N
0.2N
0.6N
1.0N

b)

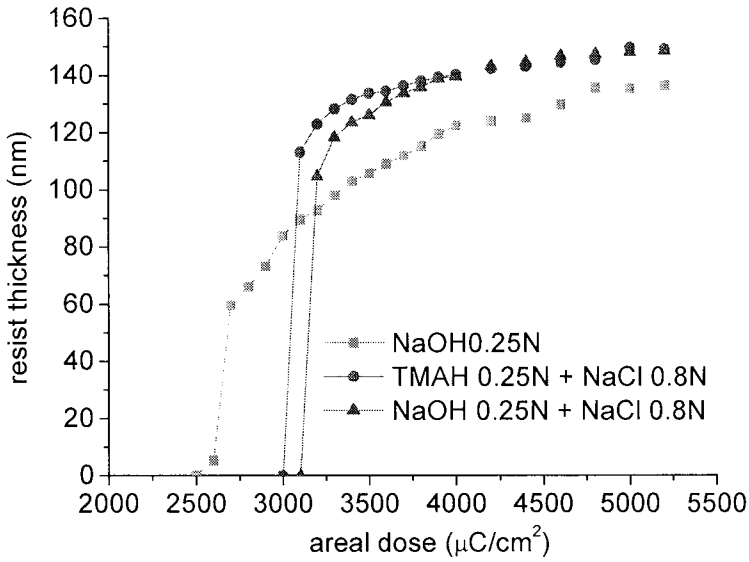

resist thickness (nm)
areal dose (μC/cm²)
NaOH 0.25N
0.2N
0.6N
1.0N

c)

Fig. 5


resist thickness (nm)
areal dose (μC/cm²)
NaOH 0.25N
TMAH 0.25N + NaCl 0.8N
NaOH 0.25N + NaCl 0.8N

a)


resist thickness (nm)
areal dose (μC/cm²)
NaOH0.25N
TMAH 0.25N + NaCl 0.8N
NaOH 0.25N + NaCl 0.8N

b)

Fig. 6