

Contrast enhancement behavior of hydrogen silsesquioxane in a salty developer

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We investigated a contrast enhancement behavior of hydrogen silsesquioxane (HSQ) in a salty development system (NaOH/NaCl). Time-resolved analysis of contrast curves and line-grating patterns were carried out to investigate the unique properties of a salty development process. The addition of salt enables a continuous development process which has not been seen in a pure hydroxide development. The continuous thinning process in a salty developer enhances the contrast of HSQ, which allows a fast collapsing behavior in HSQ line-grating patterns. During development process, salt seems to have the role of modifying HSQ by breaking network bonds preferentially, leading to a continuous development rate.

Keywords: HSQ, salty development, contrast enhancement, NaOH/NaCl

I. INTRODUCTION

Hydrogen silsesquioxane (HSQ) is a widely utilized negative-type electron beam resist material. Due to its potential for high density patterns, namely less than 10 nm-pitch structures, intensive investigations have been carried out to find an optimized process.¹ Several development techniques, such as high temperature and high concentration hydroxide developers, have been suggested to improve the electron beam resist performances including contrast (γ) and sensitivity (D_0).^{2,3} Recently, a novel development system was reported by adding salt in hydroxide

developers, which offers an outstanding γ value (> 10) for high resolution and high density patterning.⁴

Fundamental mechanisms of the cross-linking and development process of HSQ have been investigated in conventional pure hydroxide developer systems. It is known that $\equiv\text{Si-H}$ bonds of cage-like HSQ oligomers are converted into unstable silanols ($\equiv\text{Si-OH}$) by a sequential process of Si-H bond scission and hydrolysis reaction during electron beam or thermal activation. These silanols ($\equiv\text{Si-OH}$) are eventually cross-linked into network-polymers ($\equiv\text{Si-O-Si}\equiv$).^{5,6} It was reported that developers of HSQ, usually hydroxide solutions like tetramethylammonium hydroxide (TMAH), NaOH, and KOH, easily dissolve cage-oligomers preferentially to network-polymers through the following equation, $\equiv\text{Si-H}$ (cage-oligomers) + $\text{OH}^- \rightarrow \equiv\text{Si-O}^- + \text{H}_2\uparrow$.^{1,7,8} By dissolving the final product ($\equiv\text{Si-O}^-$) in developer solutions, HSQ acts as negative-type resist material in pure hydroxide solutions. However, pure hydroxide developer solution causes the remaining HSQ to be covered with an insoluble layer, which finally stops further development and prohibits an improvement in contrast.⁹ The existence of this insoluble layer is critical for the design of new development systems.

In this report, we studied a salty development process, NaOH (1wt%) / NaCl (4 wt%), which is known to have the highest contrast (γ) values among the results

reported in Yang and Berggren.⁴ In terms of the contrast enhancement behavior, we investigated the role of salt in hydroxide developer, through time-resolved analysis during development process. We compared both a salty (NaOH/NaCl) and a non-salty (NaOH) development processes using contrast curve variations and grating-line patterns. The modification of chemical bonding of HSQ by the addition of salt was analyzed with FTIR. We find that continuous development is a key property of salty developer, leading to contrast enhancement.

II. EXPERIMENTS

HSQ solution (XR1541, 6%) from Dow Corning Co. was spun on silicon nitride coated silicon substrates, to a thickness of ~ 140 nm. Pre-bake was not performed since baking process degrades the γ and the pattern resolution. Electron beam exposures were carried out on a Vistec VB electron-beam system operating at 100 keV. For contrast curve characterization, $\sim 20 \mu\text{m} \times 50 \mu\text{m}$ wedge patterns were exposed with an electron beam current of ~ 100 nA. The area doses were controlled from 1 mC/cm^2 to 10 mC/cm^2 . In the case of grating-line patterns (1 mm long), we used 40 nA electron beam current. The exposed patterns were developed by a salty solution (NaOH 1 wt%/ NaCl 4 wt%) and a non-salty solution (NaOH 1 wt%) for various times from 1 min to 16 min at room temperature. The thickness of the remaining HSQ was measured with a surface profilometer. To see the cross-sectional view of grating lines, we used a JEOL

JSM-7401F scanning electron microscope (SEM). For analysis of chemical bonding status of HSQ, Fourier transform infrared (FTIR) measurement was performed.

For the investigation of aging effects of HSQ, we used HSQ solution (XR1541, 4%) and 200 keV AIPeL system which is a projection-type electron beam lithography tool modified from transmission electron microscope (TEM).¹⁰ The remaining resist thickness was measured with an optical-measurement system (Nanospec AFT/4150, Nanometrics).

III. RESULTS AND DISCUSSION

Figure 1 shows the time-resolved contrast curves in both salty and non-salty developers. The difference in curve shape between the two developers becomes more distinct for longer development times. In the case of non-salty developer, there are no noticeable changes as the development times are varied. However, the contrast curves of salty developer continue to change as the development time increases. In order to evaluate the development process, we plotted the values of γ and D_0 as a function of development time in Fig. 2(a) and 2(b), respectively. In the case of non-salty developer, the γ decreases slightly and saturates to ~ 4 after 4 min. On the other hand, the salty developer allows γ to increase continuously, up to ~ 12 . The D_0 plot shows that the non-salty developer causes the development

process to stop after 4 min, whereas the salty developer allows development to continue.

For a more precise analysis of the development process, we plot the remained HSQ thickness during development for different electron beam doses, which provides an alternative view of time-resolved contrast curves. (Fig. 3) Interestingly, at the early stages of the development process, both salty and non-salty developers show similar behaviors, such as a sharp decrease of thickness followed by a gradual saturation. However, as the development time is further increased, the salty developer continues to thin the resist film, whereas the non-salty developer does not lead to any significant changes in resist thickness. This continuous thinning is a unique to the salty development system.

In a salty development system, the gradual saturation of the remained thickness followed by the continued thinning behavior enhances the γ significantly, which makes it different from other developers. For instance, conventional hydroxide developer such as TMAH is known to saturate and stop the development, which is attributed to an insoluble layer formation on HSQ surface.⁹ This saturation prevents further γ improvement, once γ is determined by the initial thinning at the very early stages of development. On the other hand, the salty developer for HSQ provides a continuous thinning process, leading to a time-dependant γ variation.

This continuous thinning process is typically observed in the medium range dose such as 2–2.16 mC/cm² of salty developer in Fig. 3(a). The later-stage thinning is the critical process which enhances contrast.

In order to illustrate the efficacy of the salty developer for patterned structures, we carried out time-resolved analysis for grating-line patterns.(Fig. 4) We used three different line patterns which have different line-doses, such as 46 nC/cm, 33 nC/cm, and 23.6 nC/cm. We developed them for different times from 1 min to 16 min in both non-salty and salty developers, and characterized the evolution of the surface profile with SEM cross-sectional images.

Figure 4(a) shows the high-range dose grating lines (46 nC/cm) which are partially merged, as can be seen in the cross-sectional view. As development time is increased, non-salty developer does not induce significant changes in surface profile, whereas salty developer starts to define the line structures after some period (4–8 min). Figure 4(b) shows that the medium-range dose patterns (33 nC/cm) obviously have the definition of separate lines, but the evolutions of resist profiles are quite different for salty and non-salty solutions. The non-salty developer tends to develop patterns isotropically, which is similar to an isotropic wet etching process. This process cannot improve the resolution significantly, since the height of patterns is also decreased as well as the line-width (inset of Fig.

4(b)). On the other hand, salty developer decreases the line width much faster than decreasing the film thickness (inset of Fig.4(b)). This anisotropic development comes from the high γ behavior of the salty development, which enhances patterning resolution. Figure 4(c) shows the low-range dose patterns (23.6 nC/cm) in which non-salty developer induces the gradual dissolution of line patterns whereas the salty developer leads to even faster dissolution, once the patterns start to collapse. This faster collapsing behavior of the salty developer is most likely due to the continuous thinning process.

To investigate the role of the salt in γ enhancement behavior, we assumed that the addition of salt modifies the chemical state of HSQ during development. Usually, hydroxide developers such as TMAH or NaOH are likely to form an insoluble layer on HSQ surface, which stops the development process.⁹ The insoluble layer is known to consist of siloxane-based network bonds, as confirmed by XPS and Fourier Transfer Infrared spectroscopy (FTIR).^{3,9} In order to analyze the change of chemical status during development, we carried out FTIR analysis by using annealed HSQ films.¹¹ The annealed HSQ film (400 °C for 1 hour) has noticeable network-bond peaks (1069 cm^{-1} and 830 cm^{-1}) in Si-O-Si stretch, which clearly shows the polymerization process during annealing (Fig. 5). To estimate the effect of developers, we dipped the annealed HSQ films in both non-salty and salty developers. FTIR analysis shows that the network-bond peak (1069

cm⁻¹) of salty development was less than that of the undeveloped film. An addition of salt appears to break network bonds preferentially, which may cause further thinning and further enhancement of contrast.

The importance of chemical bond state in the salty development system can be supported by studying aging effects. (Fig. 6) We prepared two samples: one is an aged sample which was developed more two weeks after spin coating followed by e-beam exposure and the other a sample for which all process (spin-coating, electron beam exposure, development, and thickness evaluation) were done within a day. In the case of the aged sample, 'two weeks' was arbitrarily chosen, and the sample was stored in air. Contrast curve variations for two development times (4 min and 16 min) are shown in Fig. 6. The curves clearly show an aging effect when using the salty developer. In the case of the non-salty developer, there was little difference between the aged sample and the immediately-processed sample. As the development time becomes longer, the development process stop for both samples. This tendency coincides with our experience that there were no significant aging effects in conventional hydroxide development (such as TMAH) even if we developed HSQ a month after spin-coating. This means that the non-salty development process is much less sensitive to resist aging. It is likely that the cessation of development when using hydroxides is related to the insensitivity to aging.⁹ In contrast, the salty development process was very sensitive to aging.

Only by developing immediately were we able to detect a continuous development process with noticeable γ enhancement behavior ($\gamma = 7.6$ at 4 min $\rightarrow$ $\gamma = 13$ at 16 min). The aged sample had low γ (5–6) and did not show any γ enhancement as the development time was extended. This sensitivity to aging might be attributed to the gradual cross-linking of HSQ in an ambient atmosphere. Cross-linking over time might inhibit the function of network-bond breaking of the salty developer. Since non-salty developer does not have any function of network-bond breaking, non-salty process seems to be less affected by the cross-linking of an aging.

IV. CONCLUSION

We have investigated contrast enhancement behavior of HSQ in a salty development system, through time-resolved analysis during development. An addition of a salt in a hydroxide solution enabled a continuous development process, unlike that of conventional hydroxide developers. The continuous thinning behavior of the salty developer is critical to contrast enhancement. Thinning over long development times was demonstrated using the analysis of grating-line patterns. FTIR analysis shows that the addition of salt modifies the chemical status of HSQ during the development process, by breaking network bonds preferentially. This chemical modification allows the resist to thin continuously and enhances the γ of HSQ.

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Figure captions

FIG. 1. Time-resolved contrast curves (1 min to 16 min) for both the salty (squares) (NaOH/NaCl) and the non-salty (circles) (NaOH) developers.

FIG. 2. The variations of (a) γ and (b) D_0 as the function of development time. The salty developer increases γ up to ~ 12 , whereas the γ of non-salty developer saturates after 4 minutes.

FIG. 3. HSQ thickness variations as development time for each electron beam dose for (a) the salty and (b) the non-salty developers. Typically, in the case of 2 mC/cm^2 , the salty process leads to the later-stage thinning. However, the non-salty process does not exhibit any noticeable further thinning.

FIG. 4. Time-resolved cross-sectional SEM analysis of HSQ line-grating patterns for the salty and the non-salty developer, for different electron beam line doses. (a) 46 nC/cm (high-range dose) (b) 33 nC/cm (medium-range dose) and (c) 23.6 nC/cm (low-range dose). HSQ grating line patterns are prepared on Si_3N_4 -deposited Si substrate to protect Si from NaOH wet etching.

FIG. 5. FTIR analysis for annealed HSQ films for salty and non-salty developers. All HSQ started with 140 nm thickness (bare HSQ) during spin coating.

Annealing process was carried out at 400 °C for 1 hour in vacuum, which shrank the thickness to 110 nm. Annealed HSQ samples were dipped in both salty and non-salty developers for 45 sec. The final thickness of developed HSQ was decreased to 80 nm (NaOH) and 70 nm (NaOH/NaCl). The FTIR peak heights were not normalized, so the relative difference in peak-heights may reflect the difference of thickness and density of HSQ films. In the salty developer, the network peak in Si-O-Si stretch is smaller than the remaining cage-bond peak.

FIG. 6. An aging effect of HSQ on the salty development system for two different samples; (a) aged HSQ and (b) HSQ in which all processes were done within a day. Only the salty development process is sensitive to an aging effect, whereas the non-salty development is not affected by aging.

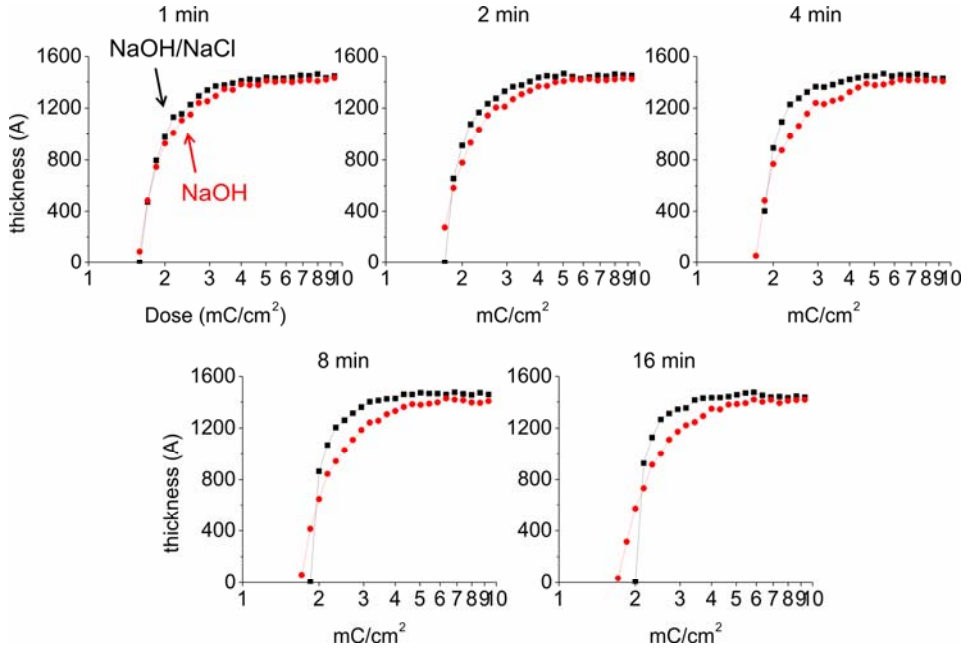


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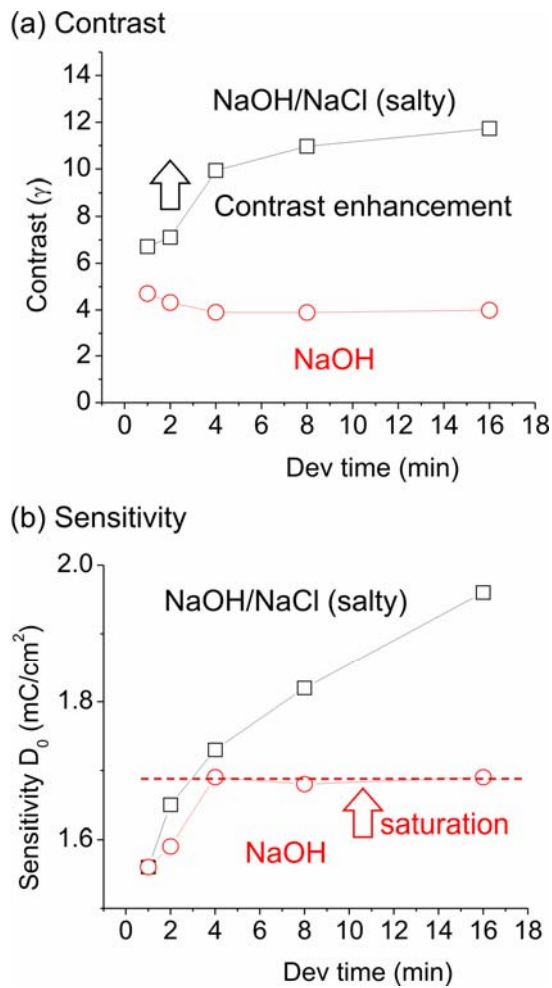


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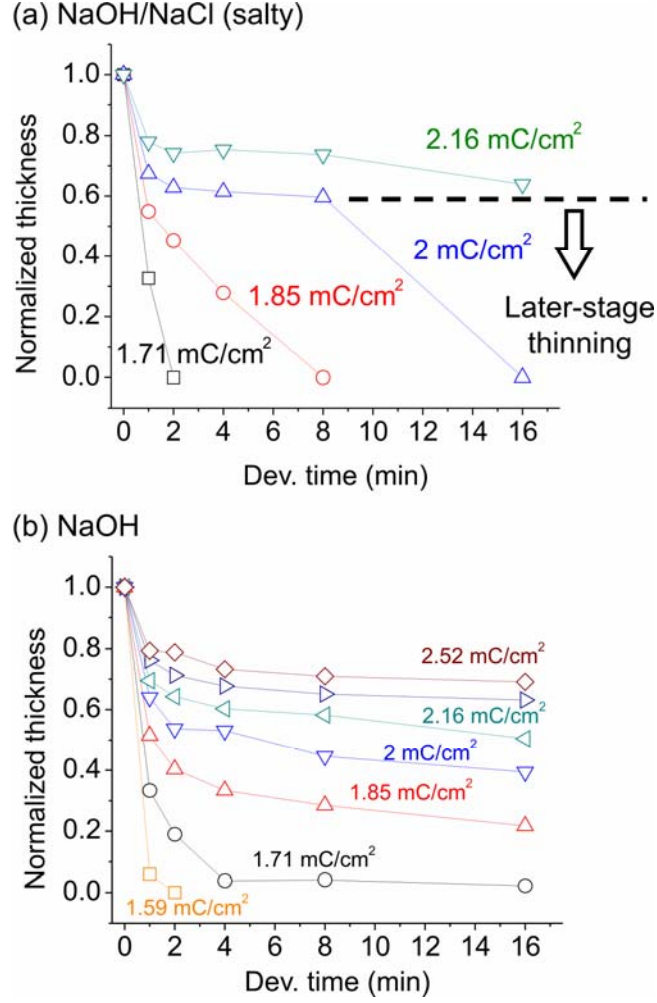
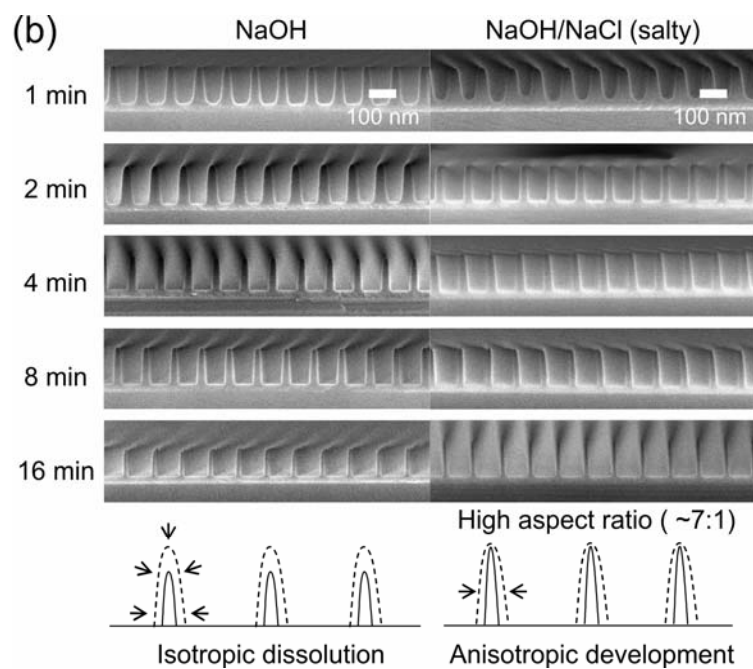
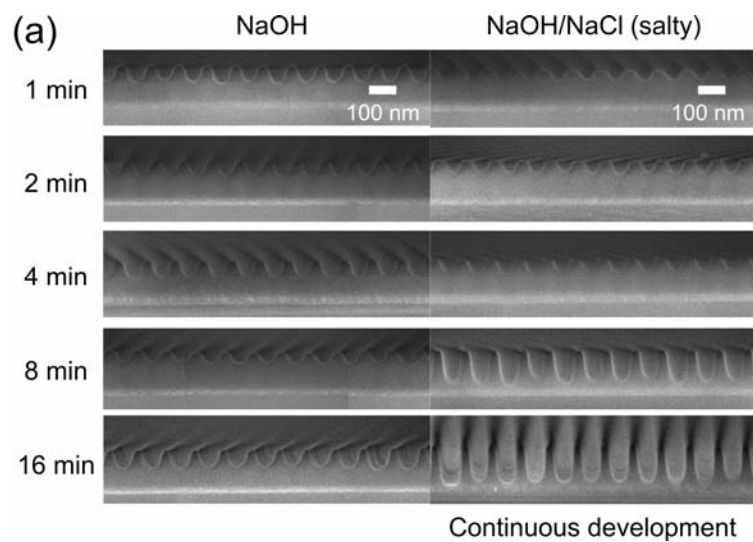


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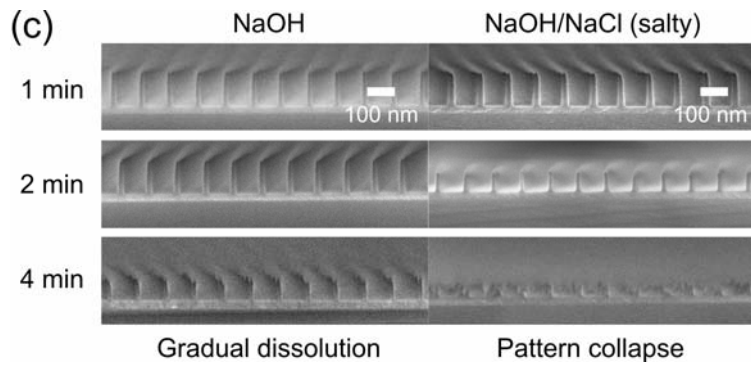


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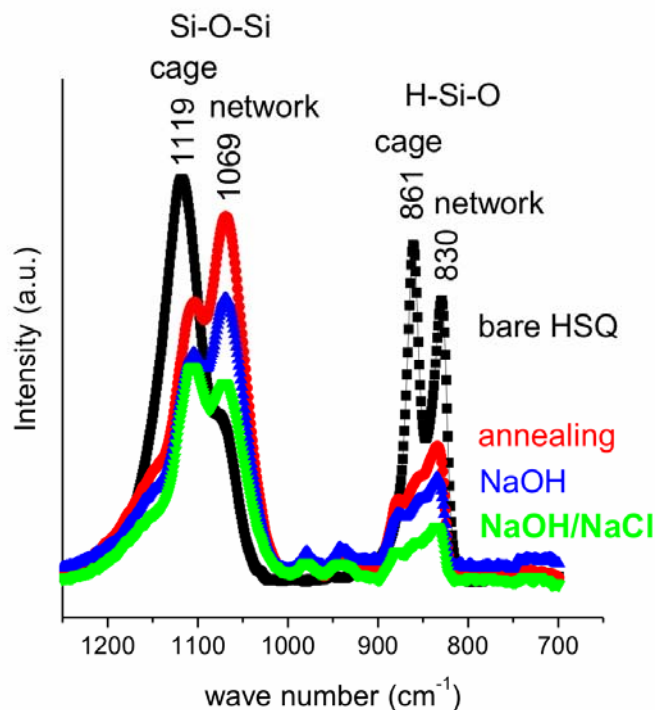


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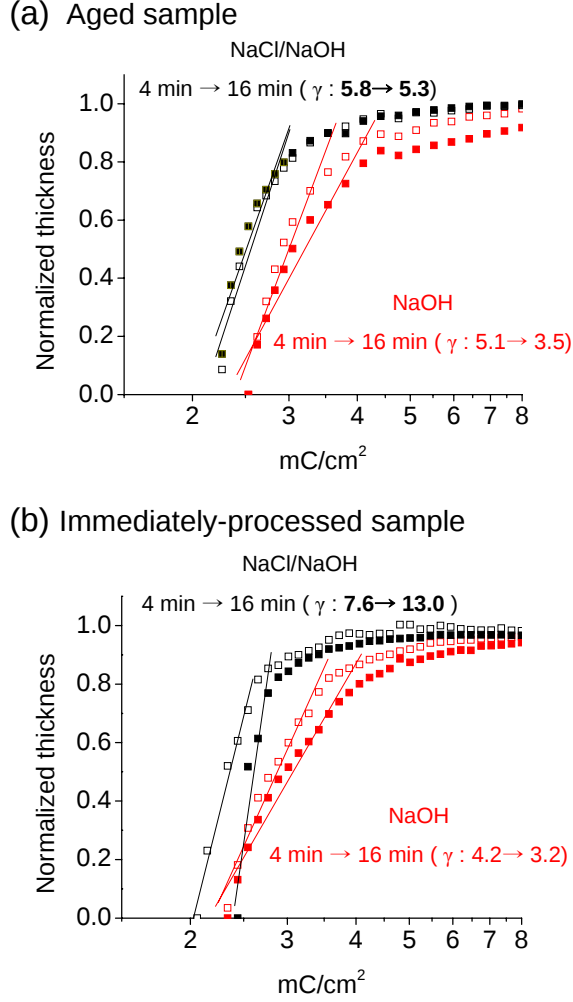


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