

Delay-time and aging effects on contrast and sensitivity of hydrogen silsesquioxane

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Hydrogen silsesquioxane (HSQ) has been shown to behave as a negative tone inorganic e-beam resist with a resolution better than 20 nm established. In this article, delay-time and aging effects on contrast and sensitivity have been investigated. The effect of a 1 week delay in air between softbake and exposure is much larger than either the aging effect or the effect of the softbake temperature. A pre-exposure delay in air seems to decrease the sensitivity and to enhance the contrast of HSQ. A general correlation between sensitivity and contrast has been established for various pre-exposure and postexposure treatments for 20, 50, and 100 kV exposures. The possible causes for the various delay-time effects are discussed. © 2002 American Vacuum Society. [DOI: 10.1116/1.1524980]

I. INTRODUCTION

Hydrogen silsesquioxane (HSQ), with composition $[\text{HSiO}_{(3/2)}]_8$ (see Fig. 1 for its structure), has been shown to behave as a high-resolution negative tone inorganic e-beam resist.¹ In HSQ, 20 nm wide 1:1 lines and spaces have been resolved using a 100 kV e beam,² and single lines less than 10 nm wide have also been reported.^{3,4} HSQ appears to be an excellent resist for testing e-beam machine resolution limits, because HSQ lines on silicon can be imaged directly in a scanning electron microscope (SEM), without the use of gold evaporation for conduction or for “liftoff” techniques. Problems with reproducing sensitivity and contrast do occur, however, when sending wafers coated with HSQ to other laboratories for testing. These problems cannot be ascribed to sensitivity of HSQ to visible light or deep ultraviolet radiation (DUV).⁵ In order to understand these phenomena, the effects of aging of the resist solution (FOX-12 from Dow Corning) and the effects of delay times, between softbake and exposure, and between exposure and development, both in vacuum and in air, have been investigated, and are presented in this article.

II. EXPERIMENT

Silicon wafers were spin coated with HSQ solutions in methylisobutylketone (MIBK) (FOX-12, Dow Corning) on a Karl Suss spinner. The FOX-12 solution resulted in a 140 nm thick layer after spinning for 10 s at 1000 rpm with closed lid. Thinner HSQ layers were obtained by diluting FOX-12 with MIBK. The HSQ layers were prebaked on a hotplate for 120 s at 120 °C, unless otherwise stated. The wafers were exposed in a Philips-Leica EBPG (4V-HR) at 20 and 50 kV with 20 pA beam current (15 nm spot size) or in a JEOL EBPG (JBX-9300FS) at 100 kV with 100 pA beam current (4 nm spot size). Test structures of crossing lines and spaces were written at various exposure doses. The wafers were developed by manual immersion at 20 °C in a 0.26 N tetra methyl ammonium hydroxide (TMAOH) developer (PD523,

JSR Electronics) for 60 s (unless otherwise stated), rinsed in 1:9 PD523:H₂O for about 5 s, rinsed in demineralized water, and blown dry with N₂. Fourier transform infrared (FTIR) spectra were recorded on a Brooker Equinox-55 in transmission mode, using a Deuterated TriGlycine Sulfate detector. Scanning electron micrographs (SEMs) were made using a Philips XL40FEG SEM.

III. RESULTS AND DISCUSSION

In Fig. 2, contrast curves are shown for 140 nm thick HSQ exposed at 50 kV. The effect of aging of the FOX-12 solution is clearly visible; this can be explained by a slow gradual oligo/polymerization of HSQ which enhances the sensitivity, but also broadens the molecular size distribution, and, hence, deteriorates the contrast. Also, the achievable resolution will be negatively affected by this gradual polymerization. In Fig. 3, the contrast and onset dose (sensitivity) are shown as a function of age of the parent FOX-12 solution. While continuously storing the FOX-12 solution at 5 °C, contrast declines with 0.1/yr and onset dose with around 7 $\mu\text{C}/(\text{cm}^2/\text{yr})$. The shelf life of FOX-12 is normally set at 6 months.

A softbake temperature above the boiling point of the casting solvent (106 °C for MIBK), generally leads to a

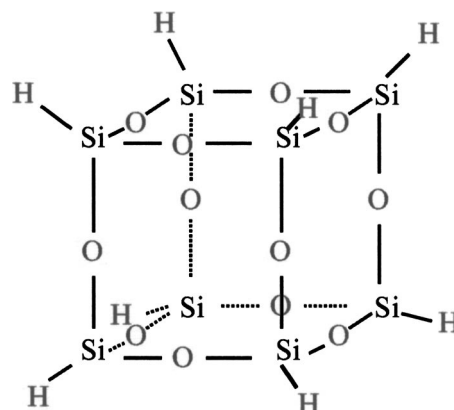


Fig. 1. Structural formula of HSQ.

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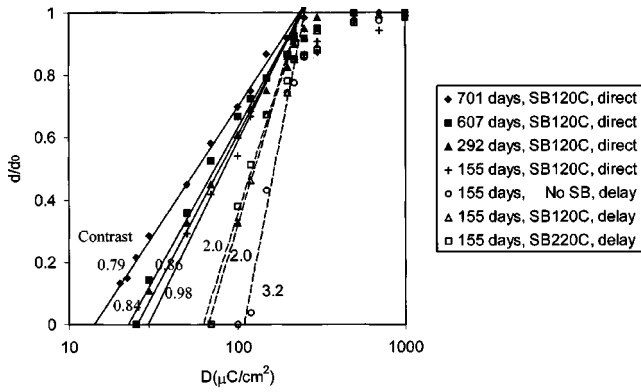


FIG. 2. Effect of FOx-12 age (days), softbake (°C) and delay (1 week in air between softbake and exposure) on contrast and sensitivity of 140 nm thick HSQ at 50 kV.

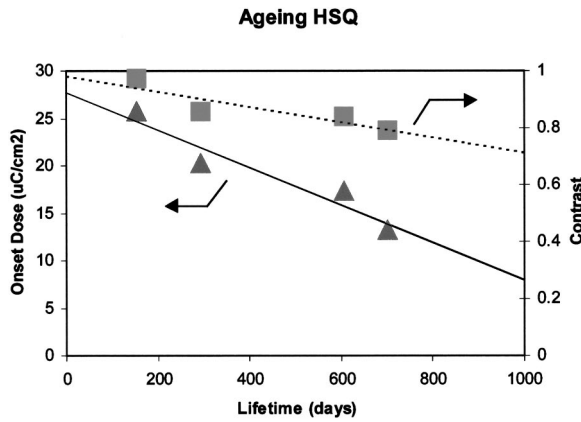


FIG. 3. Contrast and onset dose as a function of age of the FOx-12 solution (data from Fig. 2).

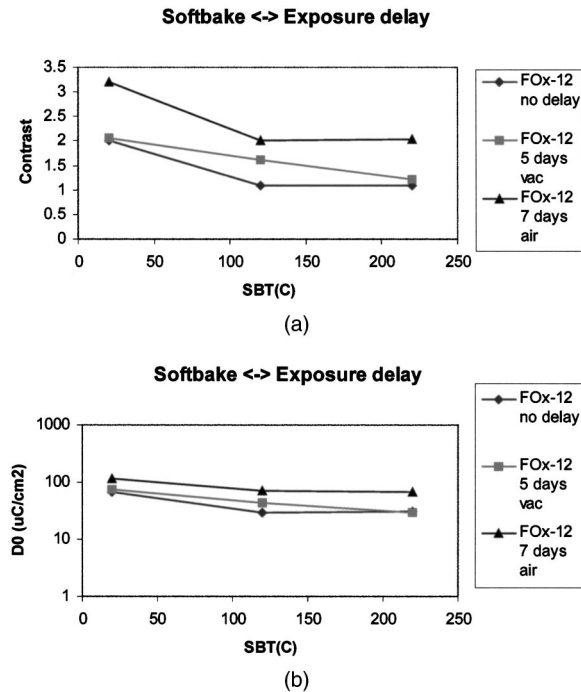


FIG. 4. Effect of the softbake temperature (SBT) and various pre-exposure delay conditions on: (a) contrast and (b) onset dose for 140 nm thick HSQ exposed at 50 kV.

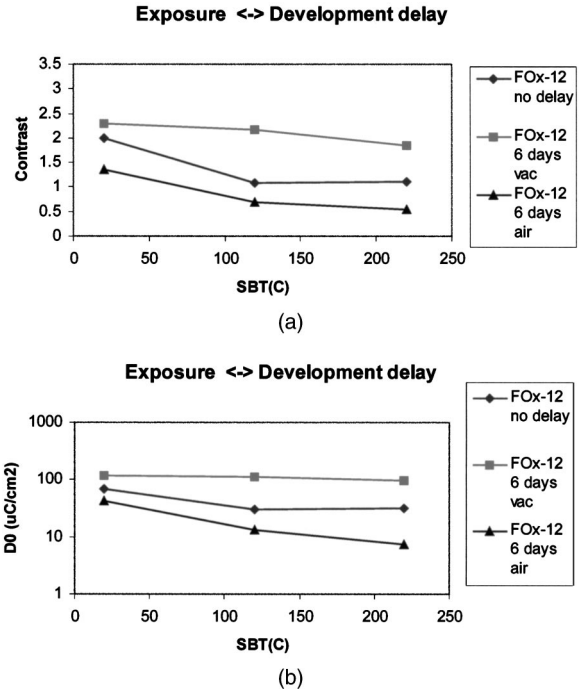


FIG. 5. Effect of the SBT and various postexposure delay conditions on: (a) contrast and (b) onset dose for 140 nm thick HSQ exposed at 50 kV.

lower onset dose and a lower contrast (Figs. 2, 4, and 5); this can be explained by a better compaction of the HSQ monomer cage molecules.

The effect of a week pre-exposure delay in air between softbake and exposure, however, is much larger than either the aging effect or the effect of the softbake temperature, as can be seen in Fig. 2. A pre-exposure delay in air seems to enhance the contrast and diminish the sensitivity of HSQ, whereas aging diminishes its contrast and enhances its sensitivity. In Figs. 4(a) and 4(b), the effect is shown of the softbake temperature and a pre-exposure delay between softbake and exposure, in either vacuum or air, on contrast, and on the onset dose (sensitivity), respectively. In Figs. 5(a) and 5(b), the effect is shown of the softbake temperature and a postexposure delay between exposure and development, in

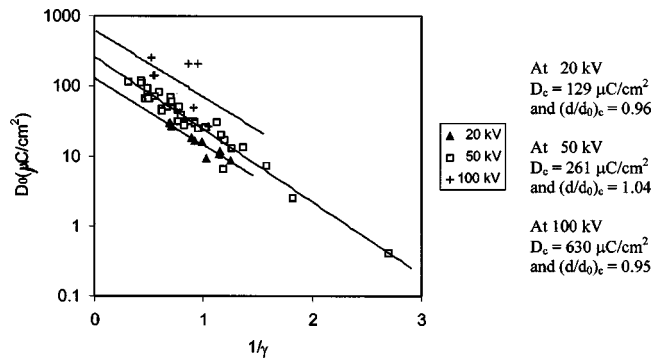


FIG. 6. Log D_0 vs the reciprocal contrast $1/\gamma$ for collected contrast curves (among others from Figs. 2–5) of 140 nm thick HSQ at various beam energies. The convergence point at $[D_c, (d/d_0)_c]$ in the contrast curves can be deduced here from $\log D_0 = \log D_c - (d/d_0)_c / \gamma$.

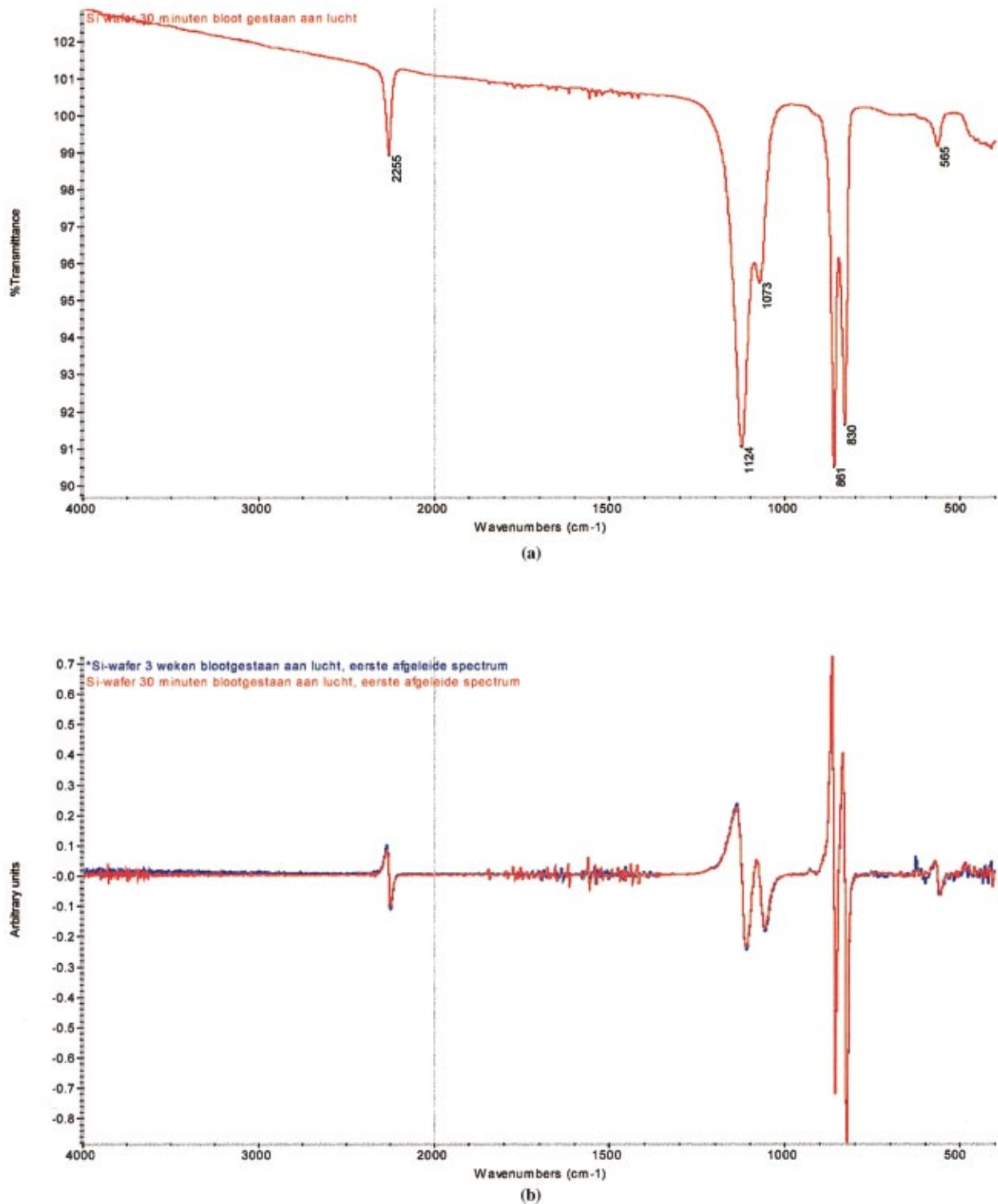
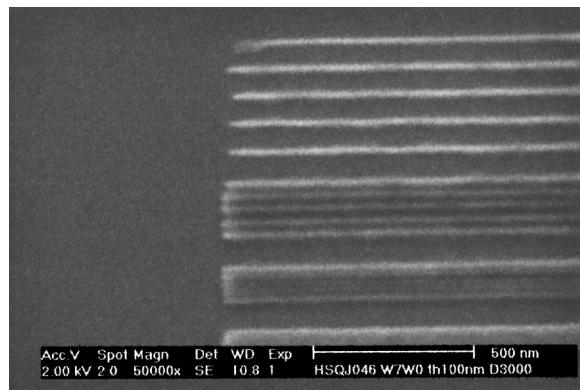


FIG. 7. FTIR spectra of a 100 nm thick layer of HSQ on a Si wafer: (a) spectrum for sample after 30 min in air and (b) differentiated spectra for sample after 30 min (red) and after 3 weeks (blue) in air.

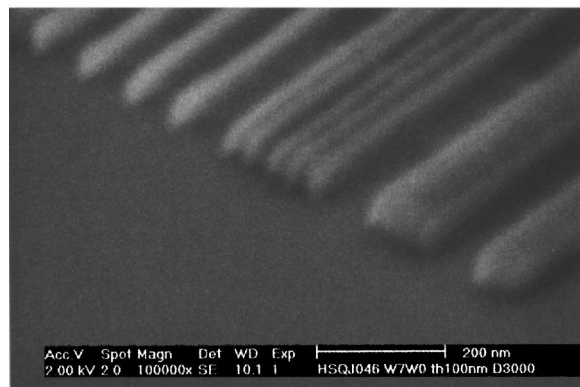
either vacuum or air, on contrast, and on the onset dose (sensitivity), respectively. The various delay effects are less easily understood than the softbake and aging effects, and will be discussed below.

Figure 6 shows that, at a given exposure energy, there is a general correlation between sensitivity and contrast for the

various pre-exposure and postexposure treatments, softbake temperatures, and FOx-12 ages. By plotting $\log D_0$ (onset dose) versus the reciprocal contrast $1/\gamma$ for all collected contrast data (among others from Figs. 2–5), a common convergence point at $[D_c, (d/d_0)_c]$ in the contrast curves can be deduced according to the equation for lines with a common



a)

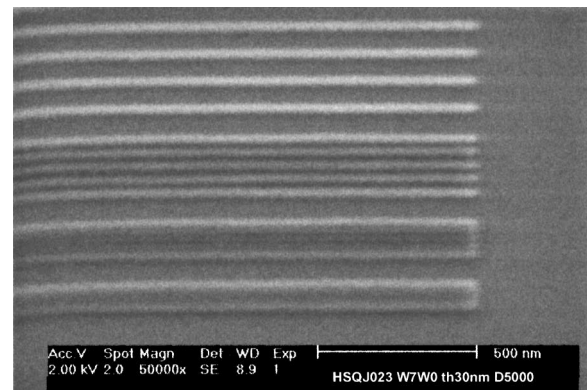


b)

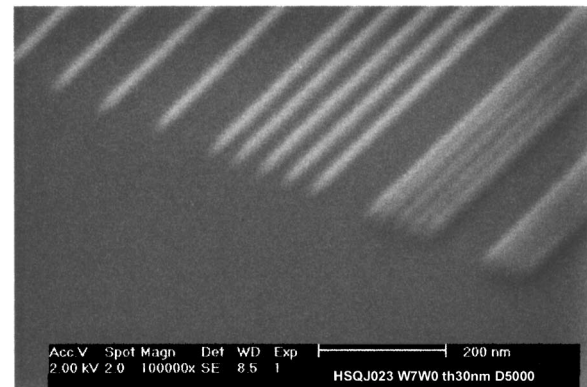
FIG. 8. SEM graphs of lines and spaces at 100, 50, 30, and 20 nm pitch in 100 nm thick HSQ written at 100 kV with $3000 \mu\text{C}/\text{cm}^2$.

convergence point: $\log D_0 = \log D_c - (d/d_0)_c / \gamma$. As $(d/d_0)_c \approx 1$ within experimental accuracy, the convergence point indicates the minimum dose needed for full “polymerization”/network formation for a given resist thickness and e-beam energy (in a large structure, taking full advantage of backscatter effects) independent of delay time and other effects. The various delay circumstances seem to affect the exposure and development in such a similar manner, that sensitivity and contrast are correlated.

The delay-time effects could be related to small amounts of contaminants, which absorb in the HSQ layer during waiting. In the chemically amplified resists, for example, small amounts of airborne ammonia and amines are known to capture the H^+ ions, generated by the photoacid generator during exposure, whose ions act as a catalyst for the polymerization or the decoupling of side groups. In order to investigate the possible role of such contaminants, FOx-12 solutions (HSQ in MIBK) have been mixed with, and HSQ layers, softbaked at 120°C , have been immersed in: an aqueous HCl solution, water, an aqueous KOH solution, 0.26 N TMAOH PD523 developer, concentrated ammonia, and diethylene triamine. The aqueous HCl solution and water do not react with FOx-12 and show hydrophobic behavior on the HSQ surface. The aqueous KOH solution and the PD523 developer react with FOx-12 under formation of gas bubbles



a)



b)

FIG. 9. SEM graphs of lines and spaces at 100, 50, 30, and 20 nm pitch in 30 nm thick HSQ written at 100 kV with $5000 \mu\text{C}/\text{cm}^2$.

and show hydrophilic behavior before dissolving the HSQ surface. Concentrated ammonia and diethylene triamine react with FOx-12 under formation of gas bubbles and fast gel formation, and show (hydro/lyo)philic behavior without dissolving the HSQ surface. Apparently, HSQ is quite stable in acid and does not readily adsorb or react with water. Hydroxide ions are responsible for the developing action of PD523. The gas bubbles can be ascribed to H_2 formation, due to the reaction of the Si-H groups in HSQ with OH^- ions. Ammonia and amines, however, absorb and react readily, resulting in network formation. In order to investigate the possible role of ammonia, FTIR spectra have been measured of an HSQ layer on Si. In Fig. 7(a), the spectrum is shown after 30 min waiting in air following the 120°C softbake. The signal at 2255 cm^{-1} is due to a Si-H stretch vibration, the signals at 565, 1124, and 1073 cm^{-1} are due to Si-O stretch vibrations, and the signals at 861 and 830 cm^{-1} are due to Si-O bend vibrations (compare Fig. 1). In Fig. 7(b), the same spectrum is shown in differentiated form, together with the spectrum of an HSQ layer after 3 weeks waiting in air. The differentiation allows us to remove background signal differences between the various silicon wafers (batch-to-batch difference in IR absorption). As can be seen in Fig. 7(b), within experimental error, there is no difference between these wafers with different delay times in air, and there is no evidence

for the occurrence of Si–N or N–H vibrations (at 3580–3380, 1175, and 900 cm^{-1}); neither is there any evidence for the presence of absorbed water or –OH groups (4000–3000 cm^{-1}).

The delay-time effects between softbake and exposure may be ascribed to a slow gradual absorption of some contaminant (not being water or NH_3), which surrounds the HSQ monomers and hampers the network formation during exposure. A slow oxidation of the Si–H groups in the HSQ monomers without network formation is not very likely and this should have also resulted in differences in the FTIR spectra in Fig. 7(b). With a delay in vacuum, the effect is almost absent, as should be expected.

The delay time effects between exposure and development are less obvious. The lowering of the onset dose in air can be explained by a slow propagation of the network formation during, e.g., oxidation. This is substantiated by the fact that the onset dose normally rises by doubling the developer time, but no longer changes if the development is repeated after 1 day of waiting in air between the two development steps. The delay effect in vacuum, however, is more difficult to understand. In high vacuum, H_2 and CO are the main contaminants. Possible explanations are acceleration of the development step by the absorbed contaminants, or a reversion of the (equilibrium) reaction forming the network due to the absence of oxygen and the presence of hydrogen. More experimental work, however, is necessary to elucidate these mechanisms.

In Figs. 8 and 9 lines and spaces are shown in, respectively, 100 and 30 nm thick HSQ as written at 100 kV in the JEOL JBX-9300FS, after 1 week delay in air between softbake and exposure. At a pitch of 30 nm, the lines are still resolved, indicating that 15 nm 1:1 lines and spaces are feasible.

IV. CONCLUSIONS

In this article, delay-time and aging effects on contrast and sensitivity of HSQ have been investigated. The effect of

a 1 week delay in air between softbake and exposure is much larger than both the ageing effect and the effect of the softbake temperature. A pre-exposure delay in air seems to decrease the sensitivity and to enhance the contrast of HSQ. A general correlation between sensitivity and contrast has been established for various pre-exposure and postexposure treatments for 20, 50, and 100 kV exposures. The possible causes for the various delay-time effects are discussed in terms of contaminant absorption and slow propagation of the network formation. For HSQ, postexposure delay should be avoided, whereas pre-exposure delay in air helps in improving contrast.

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