Nonaqueous development of silsesquioxane electron beam resist

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While the primary use of hydrogen silsesquioxane (HSQ) is as a dielectric in microelectronics fabrication, this material is also capable of forming high resolution, negative-tone features with low roughness when patterned with an electron beam. Unfortunately, under common processing conditions HSQ is relatively insensitive to electron beam exposure; poor reproducibility has also been observed. HSQ postexposure processing typically consists of development via immersion in an industry-standard aqueous solution of base, followed by rinsing with water or isopropanol. While other resist materials have been specifically designed for compatibility with aqueous base processing, HSQ is known to be chemically unstable in the presence of base. We report that several organic solvents that are not reactive towards HSQ are less aggressive at removing the exposed regions of the film. As a result, it is possible to successfully image HSQ with markedly reduced exposure dose. The considerable difference in exposure dose can be largely attributed to the difference in reactivity toward HSQ between organic solvents and aqueous base, but other factors must also be considered. For example, HSQ structures can be formed at low doses when developed with isopropanol, but the structures are very rough and irregular. This paper reports an alternative approach to HSQ processing that provides insight into mechanistic phenomena while offering certain advantages over standard processing techniques. *© 2004 American Vacuum Society.*
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I. INTRODUCTION

While the primary use of hydrogen silsesquioxane (HSQ) is as a dielectric material in microelectronics manufacturing, this material has also been found to yield high-resolution negative-tone images;[1] dense features as small as 20 nm have been reported.[2] HSQ structures have a high degree of mechanical stability and have been successfully incorporated as permanent components in diffractive optical elements[3] and templates for imprint lithography.[4] HSQ is also exceptionally resistant to oxygen reactive ion etching conditions, and bilayer schemes are capable of producing structures with overall aspect ratios that exceed 15.[2] One shortcoming of HSQ as a resist material is its relative insensitivity to electron beam exposure. Other common resists are successfully imaged with doses less than 50 $\mu C/cm^2$ at 100 kV, but HSQ often requires an exposure dose greater than 2×10^3 $\mu C/cm^2$ to obtain high-resolution patterns. The long exposure times required to deposit such a large dose limit the use of HSQ to small areas of exposure.

Previous investigations have employed common aqueous base developer solutions for HSQ processing.[1–3] Photoresists that were designed for development in aqueous base generally contain acidic functionalities that are ionized during the dissolution process via a chemical reaction with the alkaline developer solution. It has been found that the equilibrium of this acid–base reaction plays an important role in the contrast mechanism of these resists.[5,6] However, the mechanism by which acidic organic polymers dissolve in aqueous base is very different from the dissolution mechanism of HSQ.[1] HSQ functions as a negative-tone resist due to cross-linking reactions that are initiated by electron beam exposure. The increase in molecular weight that results from cross-linking decreases the dissolution rate and thus enables formation of a relief image. This molecular-weight mediated dissolution process does not require reactive, aqueous base development to produce an image.

As part of an ongoing effort to understand the mechanism of image formation in resist materials and address the lithographic limitations of HSQ, we have investigated development processing with nonaqueous solvents and solvent mixtures. While HSQ is known to be chemically unstable in the presence of aqueous base, many nonaqueous solvents are not reactive towards HSQ and can thus provide insight into the effects of any chemical reactions that occur during aqueous base development. We have found that, in general, dissolution processing of HSQ with aprotic organic solvents reduces the required exposure dose by approximately an order of magnitude. The improvement in exposure sensitivity is accompanied by a reduction in dissolution contrast by a factor of approximately 2–5, depending on which solvent is used. Consequently, it has not been possible to achieve the same resolution with solvent development that is possible with aqueous base development. Nevertheless, we have patterned dense features on a period of 124 nm with a dose of 185 $\mu C/cm^2$ at 100 kV in a 100 nm thick film of HSQ. We

have also demonstrated that solvent development of HSQ is compatible with a bilayer scheme by performing dry etch pattern transfer of a solvent-developed image into an underlying organic layer. In this paper we compare the development of electron-beam exposed HSQ in both aqueous base solutions and organic solvents as a means of investigating the dissolution mechanism of this important lithographic material.

II. MECHANISMS OF RELIEF IMAGE FORMATION

The complex behavior of HSQ can not be completely captured by any of the several general mechanisms that describe the behavior of other common resist materials. Rather, several different chemical and physical mechanisms are all active in varying degrees. The primary imaging mechanism is similar to that of other negative-tone resists; namely, exposure initiates cross-linking reactions that increase the molecular weight of the material and thereby reduce the dissolution rate. The cross-linking reactions that result from electron-beam exposure can also be initiated by thermal treatment of the film, as is routine in applications of HSQ as a dielectric material. The bake processing conditions are thus of critical importance in determining the electron beam sensitivity of HSQ. A detailed study of the relationship between bake processing and lithographic performance has been reported by Henschel *et al*.[7]

The concentration of base in the aqueous developer solution has also been reported to influence the required imaging dose.[1,7] It has been reported that the solubilization of siloxane materials is related to an ionization process[1]—a mechanism that is similar in concept to the reactive ionization process that imparts thermodynamic solubility to many positive-tone resist materials.[5] However, the role of the ionization reaction in HSQ processing is more complex than simply improving the thermodynamic affinity of the material for the solvent (although this ionization does occur and is likely a key step in the dissolution process). In addition to causing ionization of the material, aqueous base is also known to catalyze the rearrangement of Si–O–Si bonds,[8] thus creating the possibility for covalent cross-links to be both created and destroyed during the dissolution process. It is also possible for aqueous base to convert the silicon hydride functional groups that are present in the HSQ resin into silanol groups, which can react further to form Si–O–Si cross-links via a condensation reaction. The extent to which these various competing reactions affect the imaging performance of HSQ is not yet clear. In this work, we report the processing of HSQ with unreactive, nonaqueous developers and compare these results to those obtained with reactive, aqueous developers.

III. EXPERIMENT

HSQ (FOx 15) was obtained from Dow Corning (Midland, MI) as a 15% solution in methyl isobutyl ketone (MIBK), and was diluted further with electronic grade MIBK obtained from Dow Corning. Prime silicon wafers (Silicon Quest International) were cleaned with acetone, isopropanol, and deionized water and dehydrated at 170 °C for 10 min. These wafers were then cooled to room temperature, spin-coated on a Brewer Science CEE spincoater at 1000–4000 rpm, and baked on a copper plate in an oven for 5 min at 170 °C in ambient air immediately prior to exposure. Electron beam exposures were performed on a Leica VB6HR tool operating at 100 kV with a beam current in the range of 350–450 pA and a beam step size of 8 nm.

The films were developed immediately after exposure in the following solutions: LDD26W (Shipley, Marlborough MA); 25 wt. % TMAH in water (Alfa Aesar, Ward Hill MA); xylenes and acetone (Mallinckrodt Chemicals, Phillipsburg NJ); methyl isobutyl ketone (MIBK), isopropanol (IPA), and methanol (EMD Chemicals, Gibbstown NJ); *o*-dichlorobenzene (EM Science, Gibbstown NJ), and mixtures thereof. Wafers that were developed in aqueous base were rinsed in deionized water for 5 s to remove residual electrolyte left from the developer, and then dried with nitrogen. Wafers that were developed in solvent were dried without rinsing to isolate the effects of development in solvent.

Scanning electron micrographs were obtained using a LEO 1560 Gemini scanning electron microscope (SEM) operating at 2 kV at a working distance of approximately 3 mm. Thickness measurements for contrast curves were obtained using a Digital Instruments (Santa Barbara CA) Dimension 3100 atomic force microscope (AFM) operating in tapping mode, with tips obtained from NanoDevices (Santa Barbara CA). Dry etching of the bilayer samples was performed in an Oxford Instruments PlasmaLab System 100 etcher.

IV. RESULTS AND DISCUSSION

A. Developer composition

To quickly survey the effects of varying the composition of the developer, a series of HSQ films were exposed identically and then dissolved in one of nine trial developers. For purposes of comparison, one sample was developed in LDD26W, a common developer that contains a 0.26 M (2.38 wt. %) aqueous solution of TMAH. A second film was developed in a 2.7 M (25 wt. %) aqueous solution of TMAH, which Henschel *et al*. have reported to improve imaging contrast and dose repeatability.[7] (Pure water was not considered as a developer because a preliminary experiment revealed that an unexposed film of HSQ was not dissolved to an appreciable extent after immersion in deionized water for 60 s.) Development trials in methanol and isopropanol were conducted to investigate the use of alcohols as developers, while acetone and MIBK were chosen to study the use of aprotic solvents of intermediate polarity. Xylenes and *o*-dichlorobenzene were chosen to represent nonpolar solvents. Finally, a 1:3 mixture of MIBK to isopropanol was studied to investigate the performance of solvent mixtures relative to the pure solvents.

The nine samples were prepared by spincoating a 4 in. silicon wafer with a (3.6 wt. %) solution of HSQ in MIBK at 1000 rpm for 45 s. The wafer was then baked at 170 °C

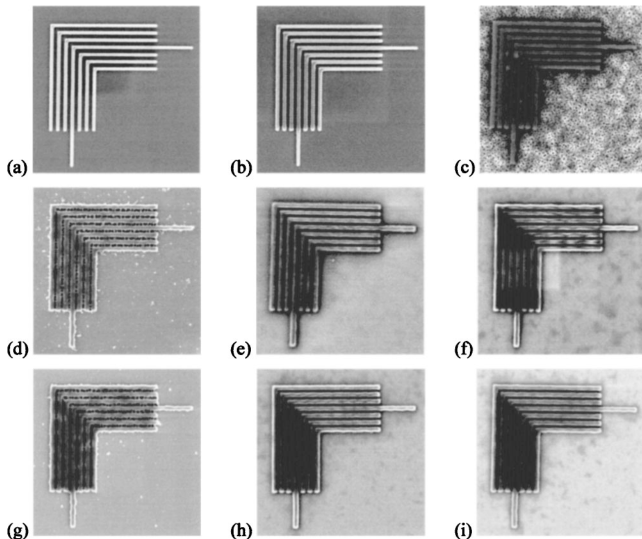

FIG. 1. SEM images of a pattern of elbows (100 nm linewidth on 200 nm period) patterned in a 100 nm thick film of HSQ and developed in several different liquids. Images shown are for the nominal "best" dose that was studied. (a) 2.7 M TMAH in water, 3.0×10^3 $\mu C/cm^2$, (b) 0.26 M TMAH in water, 1.3×10^3 $\mu C/cm^2$, (c) methanol, 1.8×10^2 $\mu C/cm^2$, (d) isopropanol, 1.8×10^2 $\mu C/cm^2$, (e) 1:3 mixture MIBK:IPA, 2.7×10^2 $\mu C/cm^2$, (f) MIBK, 1.8×10^2 $\mu C/cm^2$, (g) acetone, 1.8×10^2 $\mu C/cm^2$, (h) *o*-dichlorobenzene, 2.7×10^2 $\mu C/cm^2$, (i) xylenes, 2.7×10^2 $\mu C/cm^2$.

for 5 min, resulting in a 75 nm thick film. Nine identical arrays of elbow patterns having 100 nm wide lines were exposed on the wafer. Each array contained twelve elbows patterned in a geometric dose progression from 30 to 3.0×10^3 $\mu C/cm^2$. After exposure, the wafer was cleaved into nine pieces and each piece was immersed in one of the trial developers for 30 s.

The nominal best dose images for each of the nine developers (judged by eye for the screening purposes of this survey) are shown in Fig. 1. Development in aqueous base resulted in the best imaging performance [Figs. 1(a) and 1(b)], with the more concentrated TMAH solution producing features having exceptionally smooth sidewalls. However, this imaging performance required doses 5 to 17 times larger than the doses required for the best performance with solvent-developed samples. Aqueous base development of patterns that received less than the nominal best dose often removed all material from the substrate and therefore did not produce any image. Of the organic solvents, methanol was found to perform particularly poorly as a developer for HSQ. As seen in Fig. 1(c), immersion in methanol for 30 s did not clear the unexposed portions of the film. Subsequent experiments with methanol yielded similar results for development times of up to 240 s. Films that were developed in isopropanol were essentially cleared after 30 s; however, residue was observed near the exposed regions and the developed features were very rough [Fig. 1(d)]. The consistently poor performance of methanol and isopropanol as developers for HSQ can be understood in terms of the reported tendency of alcohols to promote gelation in HSQ.[9]

Of the two solvents of intermediate polarity, MIBK (the less polar of the two) produced smoother images than acetone, although some residual material remained outside of the patterned area [Fig. 1(f)]. Slight swelling of the remaining material was indicated by a wavy shape to the patterned lines. The lines were also wider than the nominally patterned width of 100 nm. Features developed with acetone [Fig. 1(g)] were nearly as rough as those developed in isopropanol, but subsequent experimentation on multiple samples indicated that the degree of roughness associated with acetone development was variable. No attempt was made to isolate the source of this variation, which was considered equivalent in magnitude to other processing deviations that have been reported for HSQ.

Development of HSQ in xylenes and *o*-dichlorobenzene produced features of similar quality. As seen in Figs. 1(h) and 1(i), some residual material was present after immersion for 30 s, and slight swelling is indicated by undulations in the feature sidewalls. Just as with development in MIBK, both xylenes and *o*-dichlorobenzene produced features that were significantly wider than the nominal written linewidth. The features are relatively smooth, and the best dose is much smaller than that required for aqueous base processing.

A 1:3 mixture of MIBK to isopropanol produced features that were much smoother than those developed in pure isopropanol and also resulted in less swelling than those developed in pure MIBK. It is interesting to note that the characteristic roughness observed after development in pure isopropanol was not present when isopropanol was mixed with MIBK. However, some residual material remained in the unexposed regions for this ratio of solvents [Fig. 1(e)].

A separate set of experiments was performed to measure the contrast and exposure sensitivity of HSQ when solvent developed. Acetone, methanol, isopropanol, xylenes, LDD26W, and a 9:1 mixture of MIBK to isopropanol were studied as trial developers in this set of experiments. An HSQ film was prepared as previously described and patterned with six identical arrays of 1 μm square pads exposed in a geometric dose progression from 30 to 3.0×10^3 $\mu C/cm^2$. Each exposed pattern was developed in a different developer for 30 s and then dried in nitrogen. (The sample that was developed in LDD26W was rinsed for 5 s in deionized water prior to drying.) The thickness of the material that remained after development was measured by AFM, and has been plotted in Fig. 2. Imaging contrast and exposure sensitivity were approximately the same for the several solvent developers that were studied. Development in LDD26W improved the imaging contrast by a factor of 2–5 over solvent development, while increasing the dose required for imaging by approximately an order of magnitude.

Among the nonaqueous developers studied, MIBK, xylenes, and *o*-dichlorobenzene yielded patterns of equally low roughness. Development in xylenes was chosen for further investigation because the pure hydrocarbon is not reactive toward HSQ and will not absorb a significant amount of moisture from the ambient atmosphere that might react with the HSQ material.

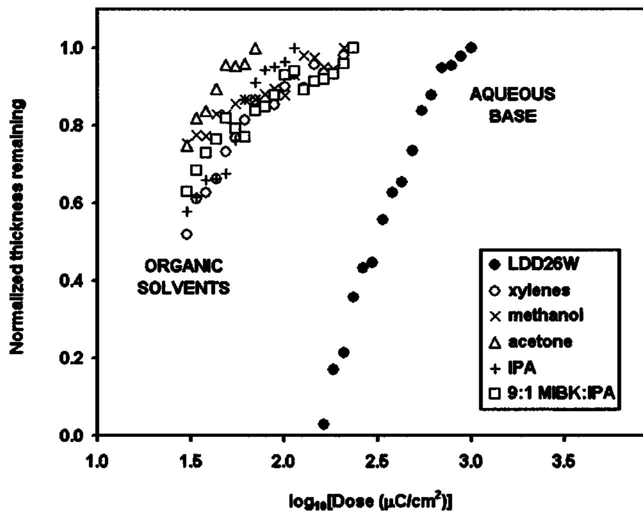

FIG. 2. Contrast curves for HSQ development with several different developers.

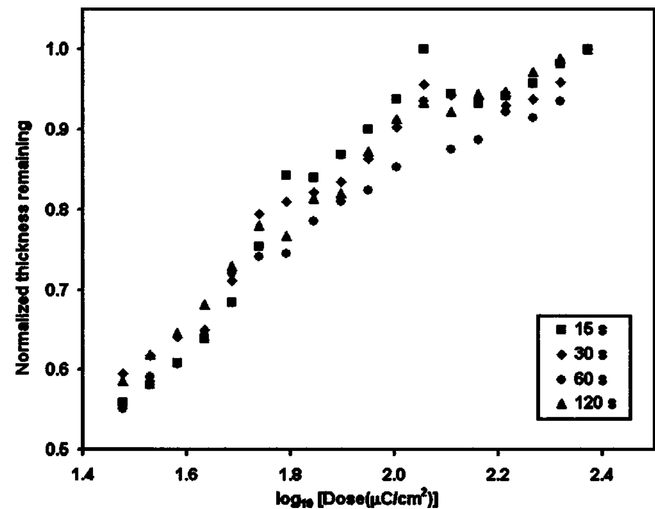

FIG. 4. Imaging contrast and exposure sensitivity for development of a 100 nm thick HSQ film in xylenes for several development times.

B. Development time

A development time of 30 s was arbitrarily chosen in the previous sets of experiments. To clarify the effect of development time on imaging performance, imaging contrast was measured for both LDD26W and xylenes for several development times. An HSQ film was prepared as previously described and patterned with eight identical arrays of 1 μm square pads exposed in a geometric dose progression from 30 to 3.0×10^3 μC/cm^2. Four samples were developed in LDD26W for times of 30 s, 60 s, 120 s, and 240 s. After development, each of these samples was rinsed for 5 s in deionized water and dried in nitrogen. Four additional samples were developed in xylenes for times of 15 s, 30 s, 60 s, and 120 s and then dried in nitrogen. Both the average thickness and the average roughness of the material that remained after development was measured by tapping-mode AFM; the results are shown in Fig. 3–6. Development of exposed HSQ in LDD26W is similar to a chemical etching process, with increasing development times in the range of 30–240 s resulting in increased removal of HSQ material (Fig. 3). Very different behavior is observed when HSQ is developed with xylenes. In this case, there is not a clear difference in the remaining film thickness when the development time varied from 15 s to 120 s (Fig. 4). Instead, any material that remains soluble after exposure is removed within the first ~15 s of immersion in xylenes.

These trends in remaining film thickness correlate with the trends in surface roughness of the remaining material. Development in both LDD26W and xylenes result in increasing surface roughness at lower exposure doses (Figs. 5 and 6). This is to be expected based on the statistical uniformity of the spatial distribution of exposure events that can result from shot noise. Surface roughness varies with development time quite differently for the two developers. For develop-

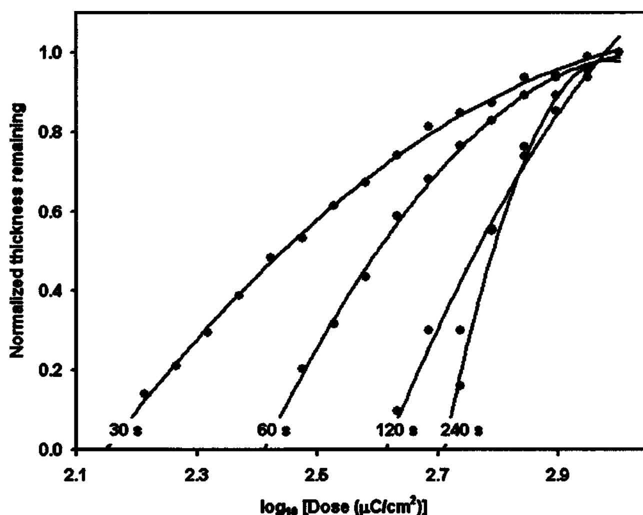

FIG. 3. Imaging contrast and exposure sensitivity for development of a 100 nm thick HSQ film in LDD26W for several development times.

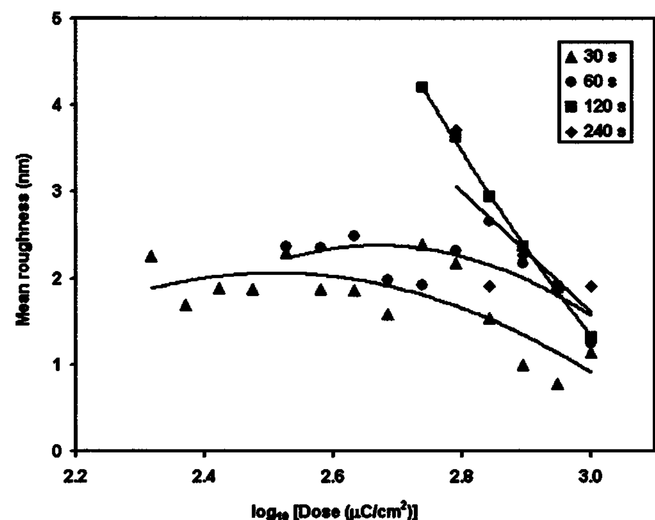

FIG. 5. Mean surface roughness of HSQ film as a function of exposure dose after development in LDD26W.

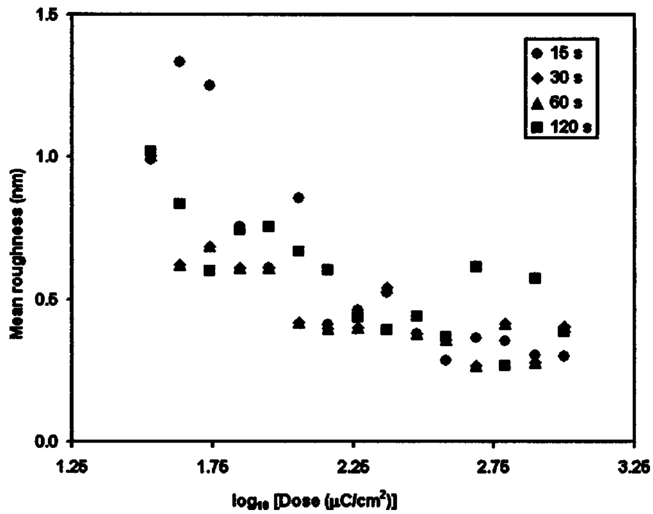

FIG. 6. Mean surface roughness of HSQ film as a function of exposure dose after development in xylenes.

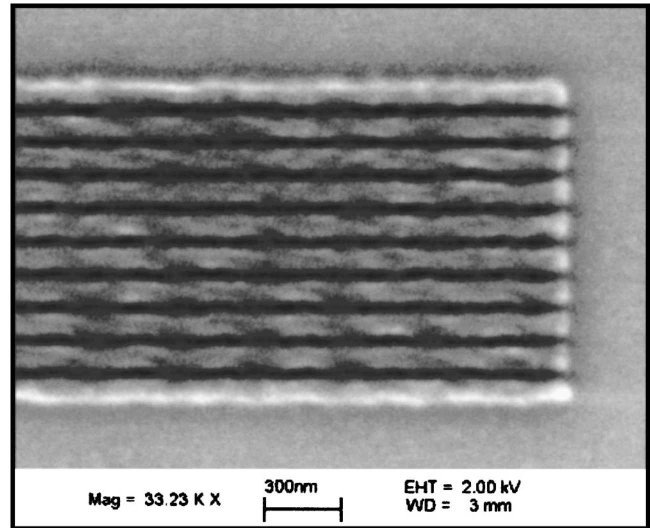

FIG. 7. SEM of dense HSQ features having a pitch of 124 nm, which were patterned at a dose of 185 μC/cm^2 and developed in xylenes.

ment in xylenes, varying the development time in the range of 15–120 s resulted in little difference in surface roughness. However, films that were developed in LDD26W exhibited an increase in surface roughness with increasing development time at a fixed exposure dose (Fig. 5). It has been previously reported that the nanoscale structure of the remaining material appears porous when imaged with a carbon nanotube AFM tip.[3] These results are consistent with a model of film dissolution by chemical etching, whereby increased etching times allow removal of regions of the film that have absorbed less exposure energy due to statistical factors. It should be noted that these trends in surface roughness of relatively large, uniformly exposed areas can not be directly translated into trends in line-edge roughness of high-resolution features. When considering development of a uniformly exposed pad of material, the high contrast of aqueous base development is responsible for the observed trend of increasing surface roughness with longer development times. However, aqueous base development of high-resolution patterns for long times has been found to reduce the line-edge roughness of the patterns. In this case, the continued etching of the film translates the edge of the developing feature to a location that received higher exposure dose, thus resulting in a lower degree of line-edge roughness after development.

C. Patterning of HSQ with solvent development

In addition to providing insight into the mechanism of HSQ development in aqueous base, development in xylenes can be used for patterning nanoscale features at markedly reduced exposure doses. A dense pattern of lines and spaces having a pitch of 124 nm is shown in Fig. 7, which has been patterned at 185 μC/cm^2 at 100 kV and developed in xylenes for 60 s. The resolution and roughness is again observed to be inferior to results obtained with aqueous base development, but the improvement in exposure sensitivity is noteworthy.

Nonaqueous development of HSQ has also been found to be compatible with a bilayer scheme, as shown in Fig. 8. In this case, a thin layer of HSQ (60 nm) is patterned at 52 μC/cm^2 on an organic underlayer (250 nm of hard-baked AZPN114, obtained from Clariant Corp.). After development in xylenes for 30 s, a brief fluorine-containing etch is used to remove residual HSQ (20 sccm CHF_3 and 30 sccm Ar at 25 mT with 20 W forward power on a 22 °C chuck for 5 min), followed by an oxygen etch to transfer the image into the underlying organic layer (10 sccm O_2 at 1.5 mT with 20 W forward power and 350 W ICP on a −100 °C chuck for 3 min).

Although HSQ has been reported to have poor reproducibility, this was not investigated in this study and we have not attempted to quantify the reproducibility of HSQ processing

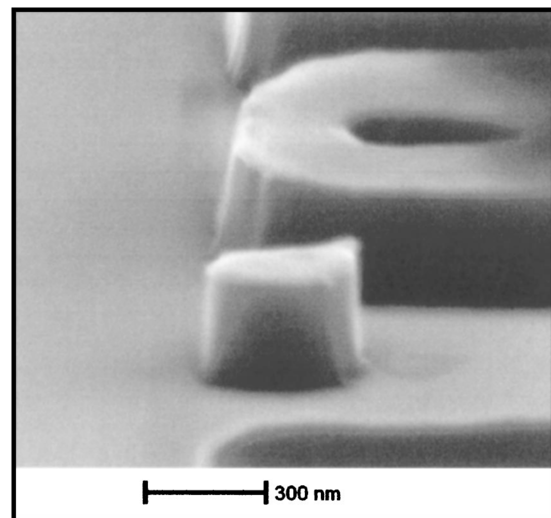

FIG. 8. SEM of a patterned bilayer consisting of a 60 nm thick HSQ layer on a 250 nm thick organic film, after development in xylenes and pattern transfer via dry etching.

with nonaqueous development. Based on our proposed mechanism of function, it is not expected that the reproducibility with solvent development would be better than development in aqueous base.

V. CONCLUSIONS

The mechanism of nonaqueous development of HSQ has been found to be fundamentally different from the mechanism by which HSQ dissolves in aqueous base. While aqueous base development can be described as a reactive etching process, the primary mechanism by which HSQ dissolves in an organic solvent is a physical (rather than chemical) process that is limited by the formation of a cross-linked network. As a result of the less aggressive dissolution process, it is possible pattern HSQ with much lower exposure doses. Although the sensitivity to electron beam exposure is much greater with organic development, both the contrast and resolution of the patterning process are noticeably reduced. Nevertheless, it has been possible to pattern sub-100 nm features in HSQ; development in xylenes enables patterning with a dose less than 200 $\mu C/cm^2$ at 100 kV. We have also demonstrated pattern transfer from a thin HSQ film into an underlying organic film.

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[1]H. Namatsu, Y. Takahashi, K. Yamazaki, T. Yamaguchi, M. Nagase, and K. Kurihara, J. Vac. Sci. Technol. B **16**, 69 (1998).
[2]F. C. M. J. M. van Delft, J. P. Weterings, A. K. van Langen-Suurling, and H. Romijn, J. Vac. Sci. Technol. B **18**, 3419 (2000).
[3]J. A. Liddle, F. Salmassi, P. Naulleau, and E. Gullikson, J. Vac. Sci. Technol. B **21**, 2980 (2003).
[4]D. P. Mancini, K. A. Gehoski, E. Ainley, K. J. Nordquist, D. J. Resnick, T. C. Bailey, S. V. Sreenivasan, J. Ekerdt, and C. G. Willson, J. Vac. Sci. Technol. B **20**, 2896 (2002).
[5]P. C. Tsiartas, L. W. Flanagin, C. L. Henderson, W. D. Hinsberg, I. C. Sanchez, R. T. Bonnecaze, and C. G. Willson, Macromolecules **30**, 4656 (1997).
[6]L. W. Flanagin, C. L. McAdams, W. D. Hinsberg, I. C. Sanchez, and C. G. Willson, Abstr. Pap. - Am. Chem. Soc. **218**, 112 (1998); G. M. Schmid, S. D. Burns, P. C. Tsiartas, and C. G. Willson, J. Vac. Sci. Technol. B **20**, 2913 (2002).
[7]W. Henschel, Y. M. Georgiev, and H. Kurz, J. Vac. Sci. Technol. B **21**, 2018 (2003).
[8]F. J. Feher, Gelest Catalog: Si, Ge, Sn, 32–45 (1998).
[9]M. J. Loboda and G. A. Toskey, Solid State Technol. **41**, 99 (1998).