Nanometer-period gratings in hydrogen silsesquioxane fabricated by electron beam lithography

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Hydrogen silsesquioxane (HSQ) is a high-resolution negative-tone inorganic resist for electron beam lithography. Investigations on the smoothness of the surfaces of thin films (less than 100 nm thick) have been conducted for nanolithography applications. It is demonstrated that films at thicknesses down to 25 nm have very low rms roughness and are defect free. Using 50 kV electron beam lithography, we demonstrate the achievement of isolated 6-nm-wide lines and 27 nm period gratings in 30 nm HSQ films on silicon substrates. These results are superior to those achieved with poly(methylmethacrylate) resist and demonstrates the versatility of HSQ for nanolithography. © *2003 American Vacuum Society.* [DOI: 10.1116/1.1629711]

Poly(methylmethacrylate) (PMMA) has served as an ultrahigh resolution organic resist for many years. Patterns with feature sizes less than 20 nm can be routinely achieved in PMMA. Broers[1] studied the resolution of PMMA as a positive resist and demonstrated 15 nm features on thin silicon nitride films using electron beam lithography at 50 kV. Craighead *et al.*[2] demonstrated features of similar sizes on thick substrates with higher electron energy. In order to achieve features substantially less than 10 nm in PMMA, Chen and Ahmed[3] utilized electron beam lithography at 80 kV followed by development in an ultrasonic bath. With this technique, they achieved minimum feature sizes between 5 and 7 nm. Also using ultrasonic-assisted development in high contrast developers, Yasin, Hasko, and Ahmed[4] have created lines in PMMA with a minimum feature size of less than 5 nm. Fabrication of gratings is another method to probe the ultimate resolution of resists. Using high-contrast developers, Thoms, Macintyre, and McCarthy[5] demonstrated lifted-off 32 nm period Ni/Au gratings while Yasin, Hasko, and Ahmed[6] demonstrated evenly spaced gratings with periods between 32 and 38 nm in PMMA resists. Both experiments utilized 40-nm-thick resists and exposures were conducted at beam voltages greater than 80 kV. It is also worth noting that as a negative resist under high electron beam dose, Tada and Kanayama[7] have demonstrated 10 nm features in PMMA. To achieve negative tone features smaller than 10 nm and to minimize linewidth fluctuations, Namatsu *et al.*[8] have developed a polysiloxane resist, hydrogen silsesquioxane, which is normally promoted as a low-*k* dielectric for semiconductor applications. Hydrogen silsesquioxane (HSQ) is an inorganic three-dimensional polymeric-type material that upon electron irradiation undergoes cross-linking via Si—H bond scission.[8] This cross-linking results in HSQ having an amorphous structure similar to SiO_2 that is relatively insoluble in alkaline hydroxide developers. Patterning HSQ with 70 kV electron beam lithography, Namatsu[9] demonstrated lines with a width of 7 nm and an aspect ratio of 10. It has also been demonstrated that HSQ responds to photon-based lithography with 50 nm resolution achieved using x-ray lithography.[10] In addition, investigations in the fabrication of HSQ gratings have been conducted. Gratings with 40 nm periodicity have been clearly resolved in 50-nm-thick HSQ that was exposed using an electron beam system operating at 100 keV.[11,12] The small molecular size of HSQ should make possible gratings with finer periodicities; indeed this has been alluded to by van Delft[12] but has not been demonstrated. Apart from its high-resolution capability, HSQ has a better dry etch resistance than PMMA which makes it a desirable resist for processing at nanometer dimensions.[13,14] Additional investigations on the ultimate resolution of HSQ are required in order to make it a versatile resist for nanometer processing.

In this Letter, we report our work on the characterization and the exposure of thin films of HSQ using electron beam lithography. The surfaces of HSQ films as thin as 25 nm were characterized and the exposure characteristics of isolated lines and ultrashort period gratings in these films have been studied. The results demonstrate that linewidths as small as 6 nm and gratings with periods less than 30 nm can be achieved using HSQ.

An HSQ solution (FOx-12) obtained from Dow Corning was diluted with methylisobutylketone (MIBK) and spun to various thicknesses on silicon wafers for the experimental work on surface characterization. The silicon wafers were first cleaned with acetone and isopropyl alcohol and then baked at 200 °C for 2 min to remove residual moisture. Next, samples were spin coated with a solution of 2:1 MIBK:FOx-12 at speeds varying from 2000 to 7000 rpm for 60 s. The samples were then baked at 120 °C for 120 s followed by a second bake at 200 °C for 120 s. The thicknesses of the resulting HSQ films ranging from 25 to 100 nm were

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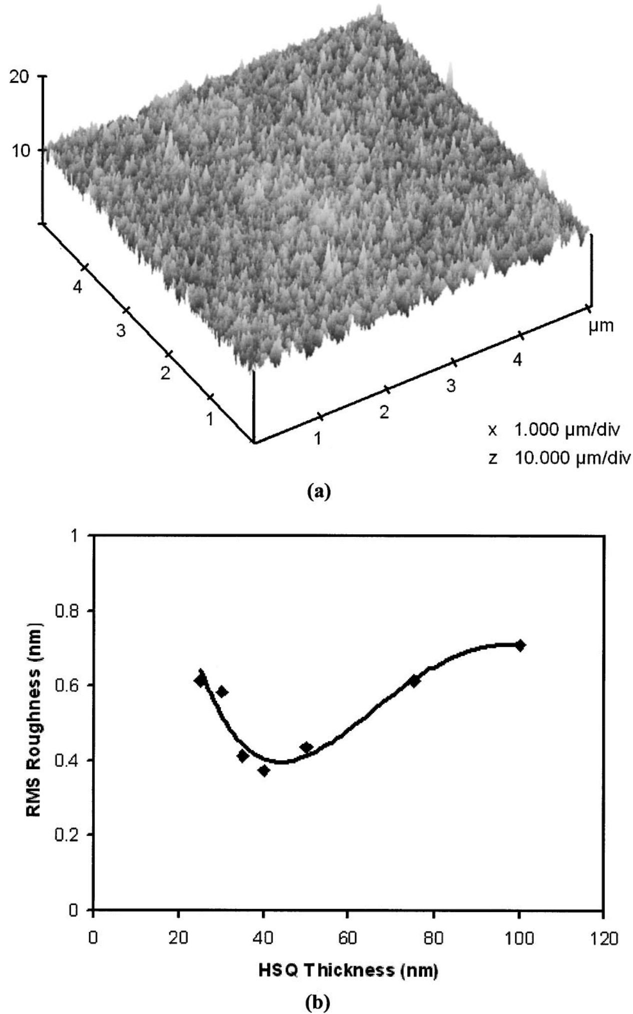


FIG. 1. (a) AFM image of the surface of HSQ at a thickness of 30 nm, and (b) rms surface roughness vs HSQ resist thickness.

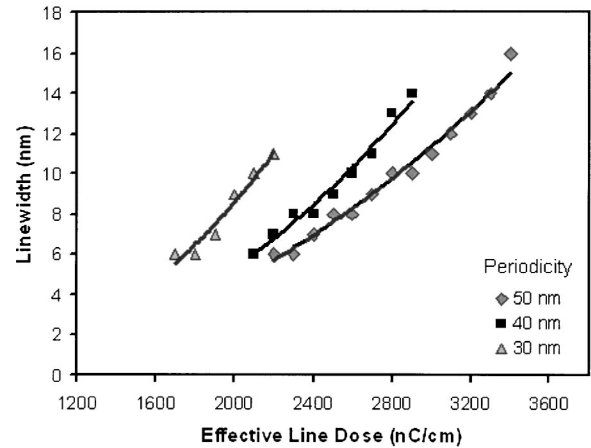


FIG. 2. Width of individual lines vs dose for 30, 40, and 50 nm gratings exposed in 30 nm of HSQ resist.

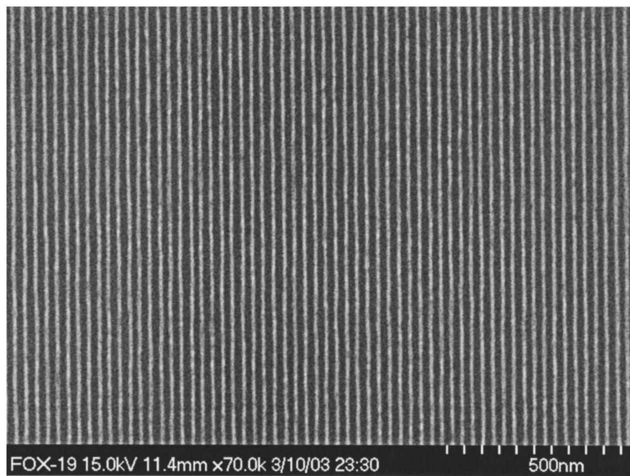
measured using a Rudolph FE-III Focus Ellipsometer. The surface topographies of these samples were examined using a Digital Instruments Dimension 3000 atomic force microscope (AFM). An ultrafine AFM probe tip with a tip diameter of approximately 2 nm was utilized for these measurements.

For our work on nanometer-scale gratings, silicon wafers were coated with HSQ films with 40 and 30 nm thicknesses, respectively. The samples were then exposed in a JEOL JBX-6000FS/E electron beam nanowriter with an acceleration voltage of 50 kV and a focused beam spot size of ~5 nm. Gratings varying in periodicity from 50 nm down to 25 nm, as well as single isolated lines (1 μm period) were written on the two samples using a double-pass technique at 20 pA beam current. Following exposures, the samples were developed by immersion in a solution of the 0.26 N tetramethyl ammonium hydroxide (TMAH) developer (MF-322 from Shipley) at 22 °C for 70 s followed by a bath in 1:9 TMAH:DI for 10 s and were then rinsed for 10 s in pure de-ionized water. After development, the samples were carefully dried using low-flow streams of N_2 gas. Following the development process, resist linewidths were measured and imaged using an Hitachi S-4700 scanning electron microscope.

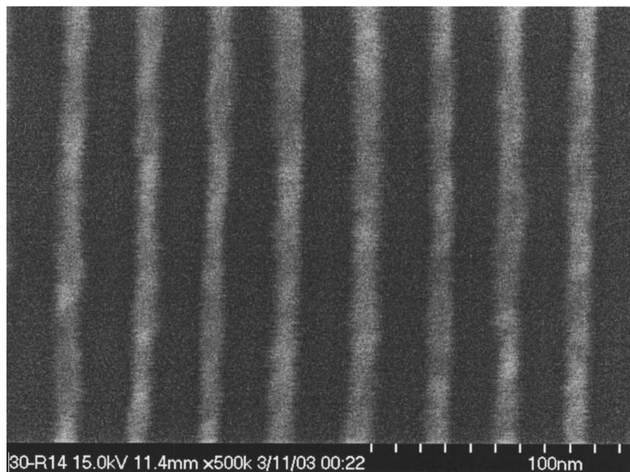
The objectives for the experiment on surface characterization were to measure the average surface roughness and to determine the presence of defects such as pinholes in the thin films. Figure 1(a) shows an atomic force micrograph of the surface of an unexposed 30-nm-thick HSQ film on silicon. No pinholes or similar defects were found in the various thicknesses (25–100 nm) of films examined. The rms roughness for the 30-nm-thick film shown in Fig. 1(a) is 0.42 nm; the rms surface roughness obtained as a function of HSQ film thickness is shown in Fig. 1(b). The maximum roughness observed at thicknesses above 90 nm is 0.7 nm while it is minimal at 0.37 nm for a thickness of 40 nm. It should be noted that the rms roughness as a percentage of film thickness is very small across the thickness range investigated. Therefore, HSQ film in the thickness range displayed in Fig. 1(b) can be safely utilized for nanolithography applications.

A contrast curve was obtained using 50 kV e-beam exposure of 120 nm HSQ film followed by TMAH development. Only a slight loss in thickness was observed at higher doses and the sensitivity of the resist was determined to be 250 $\mu C/cm^2$ at the normalized thickness of 0.8 ($D_{0.8}$) with a contrast of 2.8. These results are comparable to those obtained by Namatsu *et al.*[13] whose results were obtained at 70 kV in 100 nm resist.

Experiments on resolution limits were conducted on single layers of HSQ by exposure of gratings with various periodicities ranging from 25 to 50 nm. Exposures were performed on samples with resist thicknesses of 40 and 30 nm. An examination of the two samples showed that lines were clearly distinguishable at periods as small as 35 nm on the 40 nm HSQ sample and as small as 27 nm on the 30 nm HSQ sample. The minimum period that could be resolved depended on resist thickness; however, both samples showed similar correlations between the width of the lines and the effective exposure dose within the overlapping grating periodicities. Linewidths within the gratings increased as a function of dose. Figure 2 shows the results of linewidth as a

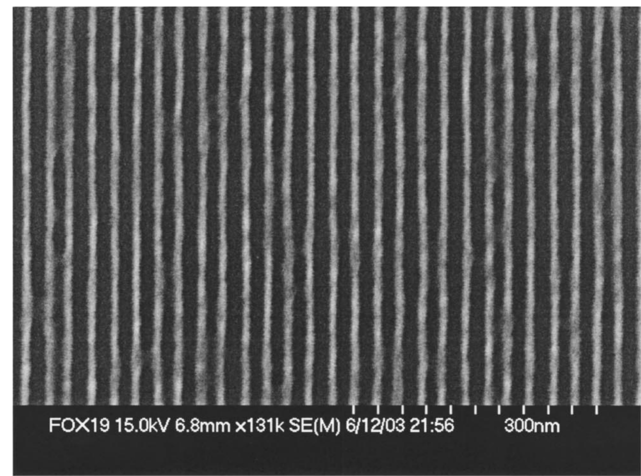


(a)

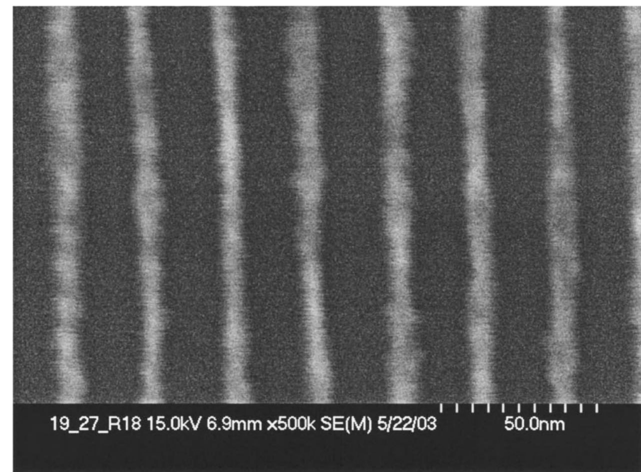


(b)

FIG. 3. 30 nm period grating exposed in 30-nm-thick HSQ resist on Si; (a) overall gratings, and (b) higher magnification view of ~10 nm lines at 30 nm period exposed at 2200 nC/cm.



(a)



(b)

FIG. 4. 27 nm period lines exposed in 30 nm HSQ resist on Si; (a) overall gratings and (b) higher magnification view of individual lines in the 27 nm period grating exposed at a double-pass line dose of 1650 nC/cm.

function of dose for various grating periodicities on the 30 nm HSQ sample. While the 50 nm period gratings were the least sensitive to changes to the line dose, the dose latitude became narrower as the grating period diminished. The dose latitude for obtaining 30 nm period gratings was limited to a line dose range of only 500 nC/cm. At higher doses, the lines were not perfectly isolated and web-like connections between the lines were observed due to proximity effects. At lower doses, lines were incomplete and exhibited gaps and other structural instabilities. In terms of ultimate resolution, we have obtained a minimum linewidth of 6 nm from both samples, irrespective of periodicity. The minimum width for isolated lines was also 6 nm. This limit may be due to the beam diameter that was estimated to be ~5 nm. Other investigators[8,9,11] have consistently obtained minimum linewidths between 7 and 20 nm in HSQ depending on the resist thickness, electron beam voltage, and writing strategy. It seems a distinct possibility that a resolution higher than the 6 nm obtained in this work could be achieved if a finer electron beam is utilized.

Although we were able to achieve 1:1 line/space gratings with a period of 40 nm on the 40 nm HSQ sample, we did not achieve exactly 1:1 line/space gratings on the 30 nm HSQ sample. However, the gratings achieved on the 30 nm HSQ sample were of excellent uniformity as demonstrated in Fig. 3. The 30 nm period grating shown in Fig. 3(a) is regularly spaced and uniform; this is further demonstrated in Fig. 3(b) with linewidths of 10 nm. The lines are relatively smooth which is a major attribute of HSQ as a resist. The resist pattern shown in Fig. 3(b) was exposed at 2200 nC/cm. As mentioned above, the smallest linewidth obtained for 30 nm period gratings is 6 nm at an exposure dose of 1700 nC/cm. The shortest period grating that we obtained in this work measured 27 nm as shown in Fig. 4. The lines in the 27 nm period grating were 6 nm in width. It should be noted that this represents the shortest period grating achieved to date using conventional electron beam exposure of resists. Melosh *et al.*[15] demonstrated 16 nm period gratings using the superlattice nanowire pattern transfer process where the periodicity was determined by molecular beam epitaxy.

In summary, we have shown that the HSQ is capable of

higher resolution than heretofore demonstrated. High resolution isolated lines measuring 6 nm in width and gratings with periodicities as small as 27 nm have been achieved. By continuing to refine exposure strategies and development procedure, and by reducing film thickness, smaller periodicities will be possible. Coupled with the excellent dry etching capabilities of HSQ, it should be possible to fabricate arrayed metallic gratings that can be utilized for molecular electronics.[15]

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