Sub-5 keV Scanning-Electron-Beam Lithography in Hydrogen Silsesquioxane Resist

Vitor R. Manfrinato, Lin Lee Cheong, Huigao Duan, Donald Winston, Henry I. Smith, Karl K. Berggren*

Research Laboratory of Electronics, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Abstract: We demonstrate 2-keV-electron-beam lithography with a resolution limit of 9 nm half-pitch for nested L’s and 13 nm half-pitch for large-area dot array, using hydrogen silsesquioxane (HSQ) as the resist. We obtained good agreement between experimental and Monte-Carlo-simulated point-spread functions at energies of 1.5, 2, and 3 keV. The long-range proximity effect was minimal, as indicated by simulated and patterned 30-nm holes in negative-tone resist.

Keywords: low-energy electron-beam lithography, low-voltage electron-beam lithography, hydrogen silsesquioxane, high resolution, proximity effect.

* Electronic mail: berggren@mit.edu

1. Introduction:

Scanning-electron-beam lithography (SEBL) at energies 30 keV and above is a well established method of fabricating sub-20-nm-pitch structures [1, 2, 3]. However, SEBL at
these high energies suffers from low throughput and long-range proximity effects. As an alternative, low-energy (sub-5 keV) SEBL exhibit five key advantages over SEBL at higher energies: (1) reduced dwell-time required for exposure (due to a much higher resist sensitivity with only slightly reduced beam current) [4, 5, 6]; (2) lower-cost and a smaller-footprint system [6, 7, 8]; (3) significant reduction in long-range proximity effects [4, 6, 9]; (4) lower probability of sample damage and substrate heating [8]; and (5) more efficient delivery of energy into ultra-thin resists and surface sensitive materials, such as self-assembled monolayers [10].

Previously, the finest pitch of adjacent lines fabricated at beam energies below 5 keV was 50 nm using calixarene [11], 60 nm with ZEP-7000 [11], and 60 nm with hydrogen silsesquioxane (HSQ) [8,12]. This range of resolution is not sufficient for applications that require high throughput and high pattern resolution, such as photomask fabrication and multiple-electron-beam lithography for integrated circuits [6, 8]. Key challenges to achieving high resolution at low electron energies are the reduced electron range, the increased broadening of the incident beam (forward-scattering), and larger spot size. To overcome these limitations, our experiments were conducted with ultra-thin (~ 15-nm-thick) HSQ and high-contrast development [13]. In addition, Monte-Carlo models have been developed [14, 15] to describe scattering of low-energy electrons. However, these models have never been tested at sub-20 nm length scales. The validity of low-energy exposure models are thus a critical question in the field.

Here we report 9-nm-half-pitch structures for nested L’s and 13-nm-half-pitch for a
large area (4 µm × 4 µm) dot array, patterned at electron energy of 2 keV. The dots at the corners of the arrays showed minimal deviation in diameter, indicating minimal long-range proximity effect. Monte-Carlo simulations of the point-spread function (PSF) at low electron energies are in agreement with experimental results. To demonstrate the expected reduced long-range proximity effect, we exposed a 2 µm × 2 µm area in HSQ, leaving a small central region unexposed. This type of structure would be extremely difficult to realize (even with proximity-effect correction) at higher energies.

2. Resolution Limit and Dose Requirements

The resolution of low-energy SEBL is expected to be lower than that of high-energy SEBL (e.g. 30 keV to 100 keV) due to increased electron scattering and larger spot size. In addition, the dose required to expose HSQ at low energies should also be much lower due to more efficient energy-transfer between the incoming electrons and the resist [5].

To experimentally determine the resolution limit of low-energy SEBL, all samples were prepared by spin-coating HSQ (1% solids XR-1541, Dow Corning) on silicon wafers (p-type Boron doped, 10-25 Ω.cm) with native silicon dioxide at a spin-speed of 6.5 krpm. The resulting thickness was determined to be ~15 nm using an ellipsometer. To prevent thermally-induced cross-linking of HSQ, which would lead to a loss in resolution, no pre-exposure bake was performed [13]. Unless stated otherwise, all exposures were carried out on a Raith 150 SEBL tool at an electron energy of 2 keV, with a 20 µm aperture, a working distance of 6 mm and a beam current of 64 pA. The samples
were then immersed in salty developer [13] for 4 min at 24° C, rinsed under deionized water for 2 min, and blown dry with nitrogen gas. The typical total processing period from spin coating to development was about 2-3 days. The fabricated structures were imaged by scanning-electron microscope (SEM) at 10 keV with ~ 6 mm working distance, and their dimensions were measured by image processing software (ImageJ).

Nested-L test structure, consisting of seven single-pixel L-shaped-lines were patterned in 15-nm thick HSQ at half-pitches from 9 to 30 nm. Figure 1 shows nested L’s at half-pitches of 9, 10, 20, and 30 nm. Although the 9- and 10-nm-half-pitch structures could be resolved, residual HSQ was present between the structures, and the single isolated lines were washed away. On the other hand, structures patterned at larger half-pitches (20 nm and 30 nm) appeared to be fully developed.

![Image](image.png)

**Figure 1.** Scanning-electron micrographs of nested L’s in 15 nm-thick HSQ exposed at 2 keV. (a) 9 nm half-pitch with a dose of 0.4 nC/cm (250 electrons/nm); (b) 10 nm half-pitch with a dose of 0.6 nC/cm (370 electrons/nm); (c) 20 nm half-pitch showing a clearly developed structure with a dose of 0.9 nC/cm (560 electrons/nm); and (d) 30 nm half-pitch with a dose of 1 nC/cm (620 electrons/nm).
As previously suggested [9], by using the ultra-thin resist (i.e., HSQ) we reduced the impact of forward scattered electrons, leading to higher resolution than seen before [8, 11, 12]. The minimum half-pitch observed (9 nm) coincided with the electron beam spot size (~9 nm), which was measured in [3]. Therefore, electron spot size may play a role in limiting the resolution.

To evaluate if we could maintain high resolution over large areas, we exposed 4 μm × 4 μm dot arrays on 15-nm-thick HSQ exposed at 2 keV, with half-pitches of 15 nm and 13 nm (~ 1 Teradot/in²), as shown in Figure 2a and 2b, respectively. The minimum half-pitch achieved was 12 nm, but the quality was poorer than the 13 nm half-pitch. A small amount of residual HSQ was present between the 13-nm-half-pitch dots, and the dots had considerable variation in diameter. In contrast, the 15-nm-half-pitch dots were uniform and without apparent residual HSQ between the dots. The dots at the corner of the arrays showed only minimal size deviation (~ 12 %), demonstrating that the long-range proximity effect was minimal at low-energy exposures, as expected.
Figure 2. Scanning-electron micrographs of a corner of a 4 μm × 4 μm dot array in 15-nm-thick HSQ, exposed at 2 keV. (a) 15 nm half-pitch with a dose of 2 fC/dot (12,000 electrons/dot) and (b) 13 nm half-pitch with a dose of 1.5 fC/dot (9,300 electrons/dot). The small deviation (~12%) in dot diameter between the center of the 15-nm-half-pitch array and the corner indicating minimal proximity effect.

The doses to fabricate both nested-L structures and dot arrays at 2 keV were much lower than the doses required at higher energies. For the nested-Ls shown in Figure 1, doses ranged from 0.4 nC/cm (250 electrons/nm) to 1 nC/cm (620 electrons/nm). Patterning the same structures at 30 keV required 6.4 (4,000 electrons/nm) to 16 nC/cm (9,900 electrons/nm), which is roughly 16 times higher than required 2 keV dose. The dot array with 26-nm-pitch in Figure 2b required 1.5 fC/dot (9,300 electrons/dot) at 2 keV and
it required 18 fC/dot (110,000 electrons/dot) at 30 keV; about 12 times higher\(^1\).

3. Proximity Effect

In high-energy (e.g., 30 keV to 100 keV) SEBL, a large background dose extends over several micrometers, due to back-scattered electrons. This long-range proximity effect is expected to be much less severe at low-energies due to the shorter electron range. However, this expectation has never been verified at length scales smaller than 50 nm, which is of key and ever-increasing importance in direct-write lithography.

To verify that long-range proximity effects are reduced at low electron energies, we measured the point-spread function (PSF) at energies of 1.5, 2, and 3 keV. Isolated dots were patterned in 15-nm-thick HSQ with single-pixel exposures followed by salty development [13]. The dots were exposed with doses ranging from 0.1 fC/dot \((6\times10^3\) electrons) to \(10^5\) fC/dot \((6\times10^9\) electrons), and the radii of the dots were measured from SEM micrographs using image processing software (ImageJ), as described in [16]. The reciprocal dot dose was then plotted versus the dot radius, and each PSF was normalized. Figure 3a compares the experimental PSFs we obtained with the PSF at 30 keV, determined in Ref [17] in 30-nm-thick HSQ.

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\(^1\) The dose comparisons made here, at 2 and 30 keV, are regarding single-pixel lines and single-dot exposures. This type of single-pixel exposures would require more dose than areal exposures, due to the concentrated electron distribution at the center of these structures.
Figure 3. The point-spread function (PSF) was obtained by plotting reciprocal dot dose versus the dot radius, followed by normalization. (a) PSF for 15-nm-thick HSQ at 1.5, 2, 3 keV and 30 keV for 30 nm thick HSQ; (b) Experimental and Monte-Carlo-simulated PSFs at 2 keV, showing good agreement.

Up to a radius of about 40 nm, the PSF is approximately the same for all energies, presumably due to the use of thin resist. Only the 1.5 keV PSF has somewhat wider beam-spreading at this sub-40-nm-range. For PSF comparison in the long-range radius,
we defined an “effective electron range”, which is as a point where the dose is $10^{-5}$ smaller than the incident dose. At this range, the deposited dose is considered negligible for all practical purposes. As shown in the Fig. 3a, this “effective range” of the electrons at 1.5 and 2 keV is less than 200 nm.

A Monte-Carlo simulation based on Refs. [14, 15] was conducted to determine if the measurements were in agreement with the modified Bethe dissipation-energy law for low-energies.

The comparison between the experimental and simulated PSF is possible because we used a development process with high contrast, thus decreasing experimental errors associated with development. We also assumed that the electron distribution generated by the Monte-Carlo simulation represented a close approximation to the cross-linking distribution. It should be noted that the PSF profile should not be significantly affected by the developer used, as long as this developer provides high contrast. Developers differ in terms of threshold dose and contrast. A threshold dose change merely scales the PSF uniformly for all radius values, but does not affect the normalized PSF. On the other hand, the contrast of a developer affects the accuracy of the measured features. The experimentally determined and simulated PSF were found to be in good agreement for energies 1.5, 2, and 3 keV. Fig. 3b is a plot of the simulated and experimental PSF at 2 keV.
There are several possible hypotheses that could explain the small observed mismatch between simulated and experimental PSFs, as seen in Figure 3b. Development contrast is one hypothesis for the PSF deviation from Monte-Carlo simulation. A high but finite contrast of the resist developer causes a broadening in the PSF, as observed in the long-range radius in Figure 3b. Additional effects that may appear in the sub-20-nm scale such as mass-transport limitation during development [18] are also a possible source of experimental deviation. PSF measurement is also imperfect, particularly for dots with smaller radius, which would be expected to have proportionally bigger errors in the PSF measurement.

To demonstrate the reduced scattering range at low energies, a challenging proximity-effect-sensitive pattern, as illustrated in Figure 4a, was used. It consisted of an almost fully exposed $2 \mu m \times 2 \mu m$ area with just a $40 \text{nm} \times 40 \text{nm}$ unpatterned area at the center. This pattern is expected to be illustrative of and sensitive to long-range proximity effects. If the background dose in the central area is less than the threshold required for HSQ to cross-link, then a hole will be present at the center of the negative-tone HSQ square. However, if the proximity effect is substantial, the center hole will be exposed by the scattered electrons and no hole will be present.
Figure 4. (a) Design of $2 \mu m \times 2 \mu m$ patterned area with $40 nm \times 40 nm$ unpatterned window at the center. (b) Normalized dose density (or areal dose) calculated at the center of the unpatterned area, by low-energy (2 keV) and high-energy (30 keV) SEBL. The exposure contrast at 2 keV is 3 times higher than at 30 keV. (c) Process latitude (diameter variation versus hole diameter) of the pattern shown in (a), considering a
5% dose fluctuation. The process latitude is higher and the diameter variation is lower for 2 keV than at 30 keV.

Figure 4b shows the normalized doses density (charge per unit area) calculated at the center of the pattern shown in Figure 4a for electron energies of 30 keV and 2 keV. The exposed area was divided into an address grid of 10 nm pitch (i.e., 200 × 200 address points) with 4 × 4 unexposed points at the center. For each point at position \((x, y)\) in the structure, the distance \(d(x, y; n, m)\) to every exposed point at position \((n, m)\) in the array was calculated:

\[
d(x, y; n, m) = \sqrt{|x - n|^2 + |y - m|^2}.
\]

For this calculation we considered radially symmetric PSFs [19]:

\[
PSF(r, \theta) = PSF(r).
\]

In order to easily manipulate the PSFs for dose distribution calculations, a fitting function was obtained for each PSF. Typical fitting functions commonly used are double Gaussian functions. Because of the high resolution and large-dose-range PSFs measured here, such fitting functions are not entirely accurate for beam energies from 2 to 30 keV. For the 2 keV PSF, we used three Gaussian functions which closely fit the PSF in the measured range. For the 30 keV PSF, we used two Gaussians plus a hyperbolic function. Physical meaning of the fitted functions is not studied in this work. Because the hyperbolic function goes to infinity for radii close to zero and we do not have any data on the 30 keV PSF for distances less than 10 nm, the hyperbolic function is only applied at 10 nm and above and goes to zero below 10 nm. The fitting parameters for the functions are provided in [20].
As described by [19], we used the abovementioned experimentally fitted PSFs to calculate the dose contribution from every exposed point (with charge $Q$) to the dose density $\delta(x, y)$:

$$\delta(x, y) = Q \sum_{n,m} PSF(d(x, y; n, m))$$

Thus, the normalized dose density was computed at every point of the pattern.

Exposure contrast, $K$, was used to quantify the proximity effects at the center of the pattern. $K$ was defined as $(\text{Dose}_{\text{max}} - \text{Dose}_{\text{min}})/(\text{Dose}_{\text{max}} + \text{Dose}_{\text{min}})$, where $\text{Dose}_{\text{max}}$ was the maximum dose present in the entire pattern and $\text{Dose}_{\text{min}}$ was the minimum dose present in the unexposed central region of the pattern. A higher $K$ allows for a larger exposure window and better pattern control. As shown in Figure 4b, the background dose at 2 keV is much lower than that at 30 keV. $K = 0.1$ for 30 keV and 0.3 for 2 keV.

We also calculated the process latitude for this pattern at 2 and 30 keV, shown in Figure 4c. For holes from 0 to 40 nm diameter, a dose variation of 5% was considered. Such dose variation translates into a variation in hole diameter. Figure 4c shows a better process latitude for 2 keV exposures than at 30 keV exposures due to the reduced long-range proximity effect. For a hole with 30 nm diameter, the 2 keV exposure has $\sim 10\%$ diameter variation while the 30 keV exposure has $\sim 40\%$ diameter variation.

A pattern similar to that depicted in Figure 4a was exposed and developed in HSQ, as illustrated in Figure 5a. Exposures were performed using 15-nm-thick HSQ, at 2 keV and $\sim 6$ mm working distance with a 20 µm aperture. The samples were then developed using
salty developer for 4 min at 24°C, rinsed with deionized water for 2 min, and blown dry with nitrogen gas. Figure 5b is a SEM micrograph of the fabricated pattern in the HSQ. The holes were 30 nm in diameter, enabling additive processing by using HSQ as resist. A more complex pattern, spelling the letters ‘EFRC’, was also fabricated (Fig. 5c) with features at the 20 nm length scale.

**Figure 5.** Holes and trenches patterned in 15-nm-thick HSQ at 2 keV. (a) Pattern consisting of 2 μm × 2 μm exposed area with 40 nm × 40 nm unexposed windows at the center. (b) Scanning-electron micrograph of closed-packed 30-nm-diameter holes in HSQ, using 10 nm step size and 0.3 fC/dot (1,860 electrons/dot). (c) Scanning-electron micrograph of ‘EFRC’ letters with a minimum feature size of 15 nm and minimal edge roughness.

Transferring high resolution patterns from resist to an underlying material is a concern for low-energy SEBL due to the thinness of the electron-beam resist. HSQ provides better etch resistance compared to other organic resists, such as poly(methylmethacrylate) (PMMA). We successfully etched 30-nm pitch lines into 60-nm thick XHRiC i-line anti-reflection coating polymer (Brewer Science), using 14-nm-
thick HSQ as etch mask [21]. The HSQ etch mask was fabricated at 2 keV. The polymer XHRiC layer was patterned using reactive-ion etching in gases oxygen and helium for 50s and with a radio-frequency power of 145W.

4. Conclusions

We have shown that low-energy SEBL is capable of patterning with high resolution and a dramatically reduced exposure dose. A resolution limit of 9-nm-half-pitch for nested L’s and 13-nm-half-pitch for large-area dot array in HSQ was achieved at 2 keV. The required dose was about one order of magnitude lower, compared to that required at 30 keV. PSFs at low-energies were experimentally determined and they were in good agreement with Monte-Carlo simulations. Using the experimental PSFs, the effective scattering range of electrons at energies 1.5 and 2 keV was less than 200 nm. The long-range proximity effects at sub-5-keV are much lower than at 30 keV, as demonstrated in the ‘hole-in-HSQ’ structures and the minimal dot diameter deviation at the corners of the large dot arrays.

The combined advantages of high resolution, high throughput and reduced proximity effects make low-energy SEBL an attractive alternative when speed and pattern uniformity are important. This technique would be useful for applications such as: 1) bit-patterned media; 2) fabrication of nanoimprint molds; 3) photomask manufacturing; and 4) multiple-electron-beam lithography for integrated circuits manufacturing [6, 8]. With
its more efficient energy transfer, low-energy SEBL is also useful when patterning ultra-thin and surface-sensitive materials [10].

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6. References

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[20] The point-spread function at 30 keV was fitted with the following model: 

\[ PSF_{30\text{ keV}}(r) = \frac{1}{\pi(1+\eta+2\ln\frac{\beta}{\alpha})} \left[ \frac{1}{\alpha^2} \exp\left( -\frac{r^2}{\alpha^2} \right) + \frac{\eta}{\beta^2} \exp\left( -\frac{r^2}{\beta^2} \right) + \tau \frac{1}{r^2} \right] \]

with fitting parameters: \( \alpha = 9.5 \text{ nm}; \beta = 3100 \text{ nm}; \eta = 4; \tau = 0.2 \) [17]. The hyperbolic term \( \frac{1}{r^2} \) was set to zero for radii smaller than 10 nm. The point-spread function at 2 keV was fitted with the following model: 

\[ PSF_{2\text{ keV}}(r) = \frac{1}{\pi(1+\eta+\gamma\tau)} \left[ \frac{1}{\alpha^2} \exp\left( -\frac{r^2}{\alpha^2} \right) + \frac{\eta}{\beta^2} \exp\left( -\frac{r^2}{\beta^2} \right) + \frac{\gamma}{\gamma^2} \exp\left( -\frac{r^2}{\gamma^2} \right) \right] \]

with fitting parameters \( \alpha = 10 \text{ nm}; \beta = 40 \text{ nm}; \gamma = 69 \text{ nm}; \eta = 1.5; \tau = 0.3. \)