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Proton Beam Writing of Three-Dimensional Nanostructures in Hydrogen Silsesquioxane

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ABSTRACT

Proton beam writing (p-beam writing) is a promising new direct-write lithographic technique for three-dimensional nanofabrication. In p-beam writing a megaelectronvolt proton beam is focused to a sub-100-nm spot size and scanned over a suitable resist material. Unlike electrons, when a proton beam interacts with resist it follows an almost straight path resulting in high aspect ratio structures with vertical, smooth sidewalls. The secondary electrons induced by the primary proton beam have low energy and therefore limited range, resulting in minimal proximity effects. Hydrogen silsesquioxane has been identified as a superior resist for p-beam writing, allowing the production of high-aspect-ratio structures down to 22 nm.

Hydrogen silsesquioxane ($HSiO_{3/2})_8$ (HSQ), from Dow Corning, has been shown to function as a high-resolution negative tone e-beam resist.[1,2] In HSQ, below 20 nm resolution has been reported[3] and single lines down to 7 nm wide have also been observed.[4,5] Recently it has been shown that HSQ can also be used as an extreme ultraviolet (EUV) resist using 13.4 nm wavelength,[6] and high-density 26 nm wide lines have been demonstrated. Typical contrast reported for HSQ ranges from 0.55 up to 3.2 for HSQ for e-beam writing.[3,7,8] For EUV a contrast of 1.64 has been reported.[6] Low-energy He^+ ions (75 keV) have also been used, although the imaging properties of these low-energy ions have not been reported.[9] Preliminary findings on proton beam writing (p-beam writing) in HSQ suggest great potential.[10] In this study we present the first results on high-energy p-beam writing in HSQ resist at the 20 nm level.

P-beam writing has been developed at the Centre for Ion Beam Applications (CIBA) in the Physics Department of the National University of Singapore.[11,12] This technique employs a focused megaelectronvolt proton beam scanned in a predetermined pattern over a suitable resist (e.g., PMMA, SU-8, or HSQ), which is subsequently chemically developed. The sample is mounted on a computer-controlled Burleigh Inchworm EXFO XYZ stage which has a travel of 25 mm for all axes with a 20 nm closed loop resolution. The system has been designed to be compatible with Si wafers up to 6 in. During exposures the beam is scanned over the resist in a digitized pattern using a set of electromagnetic scan coils. In this way scan fields up to 0.5×0.5 mm^2 can be achieved. The scan system utilizes a National Instruments NI 6731 Multi i/o card which has four 16-bit digital to analog converters (DACs) and has a minimum update time of 1.0 μs. To expose larger areas such as long waveguides, a combination of stage and beam scanning can be employed. Since a magnetic scanning system has a relatively long settling time due to the magnetic scan coils resulting in a relative slow writing speed, we introduced a prototype electrostatic scanning system to allow us to reduce exposure times. With this electrostatic scanning system, writing speeds comparable to e-beam writing were obtained.[13] The ability to stitch fields will be included in the second generation electrostatic scanning system. Further details of the p-beam writing setup can be found in ref 14.

The slowing-down and ensuing energy deposition of energetic charged particles (e.g., megaelectronvolt protons) impinging on and penetrating into solids is governed by the Coulomb interaction of the incident particle with the electrons and nuclei of the target. In e-beam writing as well as p-beam writing, the energy loss of the primary beam is dominated by energy transfer to substrate electrons. Unlike the high-energy secondary electrons generated during e-beam writing, secondary electrons induced by the primary proton beam have low energy[15,16] (typically less than 100 eV). The secondary electrons therefore have limited range, resulting in minimal proximity effects. In e-beam writing it is suggested that the cross-linking of HSQ is initiated via Si−H bond scission.[1] In EUV an increased sensitivity has been found for exposure with shorter wavelengths, assumed to be related to the ability to break the Si−O bonds.[9] In p-beam

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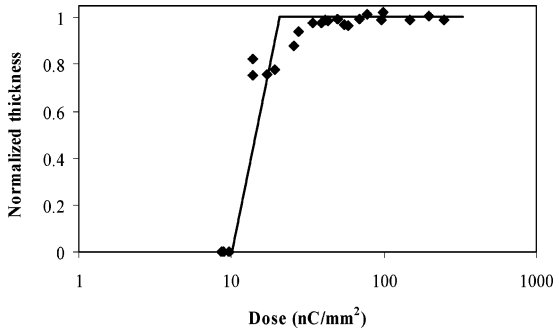

Figure 1. Contrast curve for 850 nm thick HSQ, exposed to 2 MeV protons. The straight line corresponds to a contrast of 3.2.

writing the induced secondary electrons can break either the Si−O bond (bond strength 8.95 eV) or the Si−H bond (bond strength 4.08 eV).[9] It is therefore assumed that the cagelike HSQ structure is broken and a network is formed through cross-linking via similar mechanisms to those observed in e-beam writing and EUV irradiation of HSQ.

The low proximity effects exhibited by megaelectronvolt protons coupled with the straight trajectory and high penetration of the proton beam in resist material enables the fabrication of high-density three-dimensional (3D) micro- and nanostructures with well-defined smooth side walls.[17] No proximity effects have been observed in preliminary p-beam writing experiments.[11] Up to now the only resists compatible with p-beam writing which have demonstrated sub-100-nm features are PMMA and SU-8. Other resists such as PMGI,[18] Diaplate 133,[19] and a resist based on epoxy and poly(hydroxystyrene) polymers[20] have been investigated for their effectiveness in combination with p-beam writing, but so far none of these resists have exhibited sub-100-nm resolution. In this paper, we present the first results on p-beam writing using HSQ resist down to the 20 nm level, which is currently the best performance in p-beam writing.

In this study with p-beam writing on HSQ, a thick and a thin layer are evaluated. One silicon wafer was coated with a 850 nm thick layer of HSQ (Fox-17, Dow Corning) by spin coating on to the silicon wafer for 30 s at 3000 rpm. A second wafer was coated with 100 nm of HSQ, where the Fox-17 was diluted with methyl isobutyl ketone (MIBK) (2:3 by volume respectively) and spin coated for 30 s at 3000 rpm. Both wafers were prebaked for 120 s at 150 °C before the proton beam exposure. After proton exposure the samples were developed in a 2.38% tetramethylammonium hydroxide (TMAH) solution for 60 s. The contrast curve for the 850 nm layer was measured and is shown in Figure 1. Squares of $5 \times 5\ \mu m^2$ were written with a focused 2 MeV proton

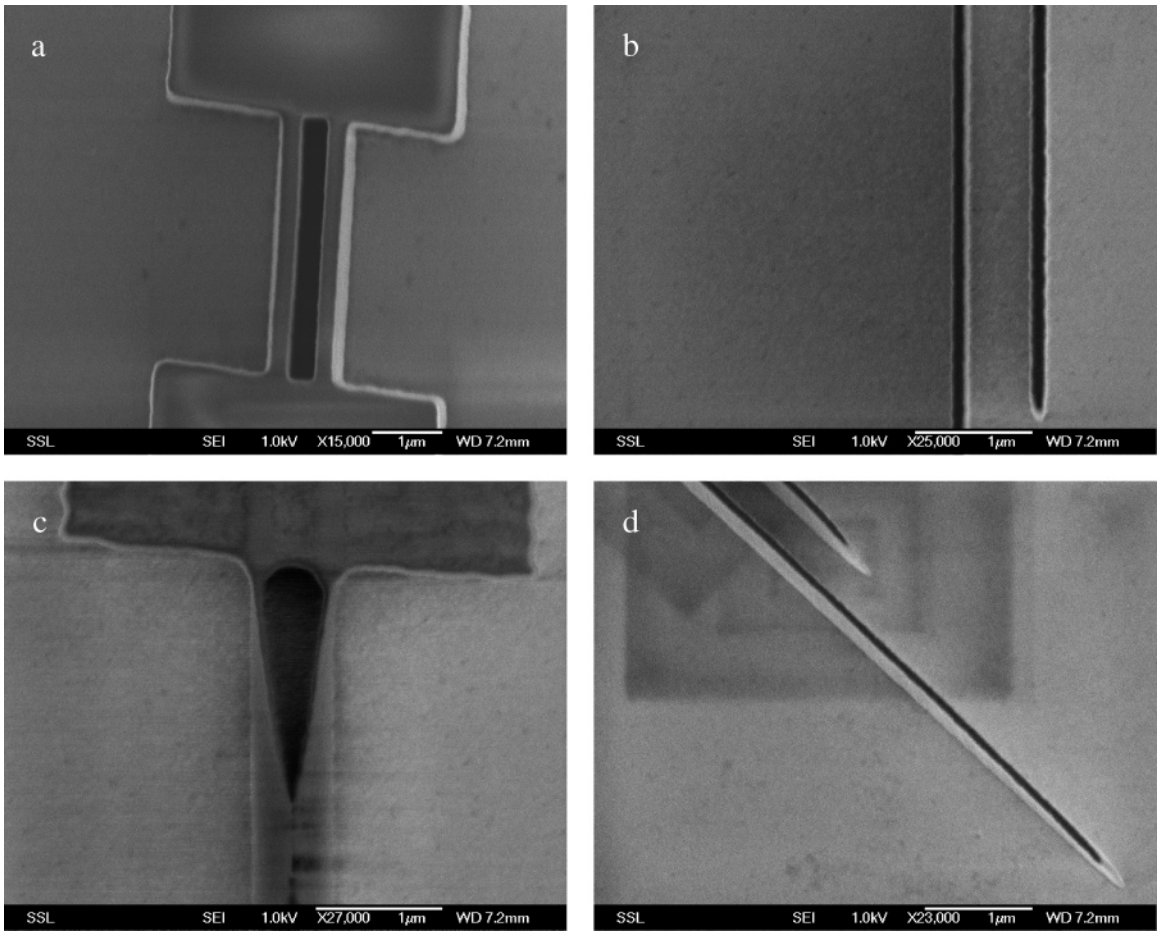

Figure 2. SEM images of parallel lines written with a 2 MeV H_2^+ beam using a nine pixel wide exposure pattern in (a) 2 μm thick SU-8 and 850 nm thick HSQ with (b) 2.4×10^6 protons and (c) 1.6×10^6 protons. In (d) 2.0×10^6 protons are used in a seven pixel wide exposure pattern.

beam, the dose was varied from 10 to 250 nC/mm^2. The height of the squares was determined with atomic force microscopy (AFM) in tapping mode. A contrast of 3.2 was found for p-beam writing. Here the contrast is defined as $\gamma = 1/[\log(D_f) - \log(D_i)]$, where D_f is the dose at which the resist is fully insoluble and D_i the dose where the resist becomes insoluble. Similar contrast values have been reported for e-beam writing in HSQ.[3,7] We define the sensitivity as the point where the layer is fully insoluble and reaches the maximum thickness, and for protons on HSQ we have measured a sensitivity of 30 nC/mm^2, similar to the sensitivity found for SU-8 exposure with protons.[18] This definition for sensitivity is used since a lower exposure dose was found to result in weaker HSQ structures. A more detailed study is planned since it was reported that the sensitivity and contrast of HSQ also change as a function of delay between the different process steps.[7]

In the next experiment, sets of two parallel lines were written with a focused 2 MeV H_2^+ beam using the same exposure pattern; one set was written in SU-8 (2 μm thick) and one set in HSQ (850 nm thick). Each set of two lines was digitized using 4096 × 4096 pixels in a writing field of 100 × 100 μm^2, where each line is nine pixels wide (corresponding to 220 nm). The fabricated lines in SU-8, 230 nm wide, have a similar width compared to the intended exposure pattern (see Figure 2a). Here a dose of 41 nC/mm^2 was used. However, the lines in HSQ are 100 nm wide and less than half the width of the exposure pattern (see Figure 2b). These narrower lines have been fabricated with a corresponding fluence of 2.4 × 10^6 protons over a total exposure area of 4.3 μm^2. By decreasing the proton fluence to 1.6 × 10^6 protons, we achieved an even narrower line (60 nm), see Figure 2c, although these lines were not sufficiently rigid and fell over during development, presumably due to capillary forces. Writing lines under similar exposure conditions but without supporting buttresses resulted in total collapse, although this did enable us to measure a wall height of 730 nm, less than the expected height of 850 nm. This is consistent with the data in Figure 1, implying that the "effective" dose in this case is less than D_f.

In a further experiment, the width of the lines was reduced to seven pixels in the exposure pattern. Administering a fluence of 2.0 × 10^6 protons over a total exposure area of 3.3 μm^2, two 40 nm wide free-standing lines were successfully exposed and developed (see Figure 2d). Currently the smallest structures in HSQ achieved with p-beam writing were written in a similar way as the previous examples by reducing the number of pixels to three per line in the exposure pattern (1.4 μm^2); see Figure 3. Here a fluence of 1.2 × 10^6 protons was used to expose the pattern. After development, a line width of 22 nm was observed. This corresponds to an aspect ratio of 39:1 (height:width). The wall is slightly tilted due to capillary forces during development. Down to the 20 nm level, we have shown that by exposing HSQ with a sufficient proton dose, the walls remain standing without the use of supercritical drying necessary for successful development of e-beam written HSQ structures.[5]

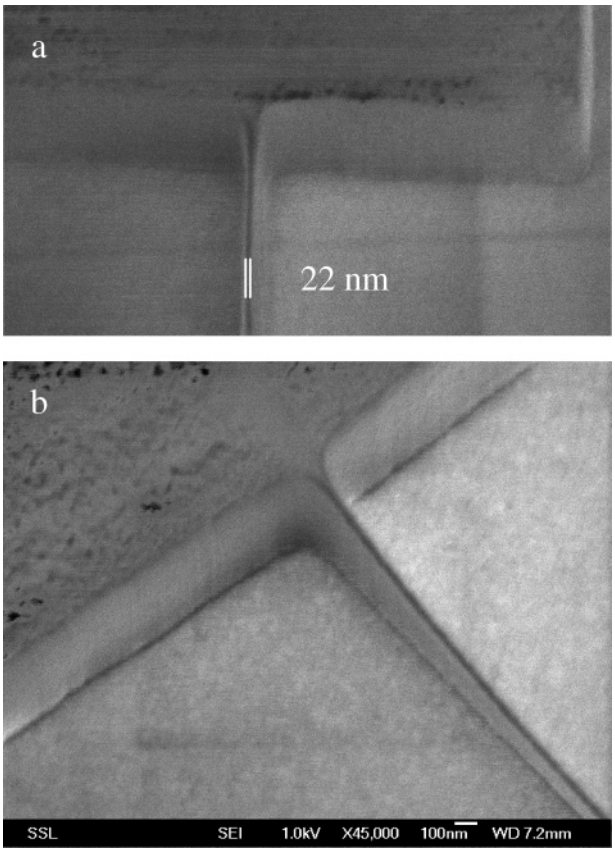

Figure 3. SEM images of a 22 nm wide line written with a 2 MeV H_2^+ beam using a three pixel wide exposure pattern in 850 nm thick HSQ with 1.2 × 10^6 protons.

In our experiments the proton beam was measured to be 100 nm in width (at $\pm 2\sigma$) following the procedure described by van Kan et al.[14] However, the resolution standards used to determine the proton beam size have a side wall slope equivalent to about 30 nm, giving rise to inaccuracies in both the beam size and beam shape determination. It has been reported that there is an increase in brightness in particle accelerators near the paraxial region.[21] To explain the discrepancy between the measured width of the proton beam and the measured line width of the lines fabricated in HSQ, we have to assume that the lateral beam spot energy density profile is peaked at the center, and due to the sharp contrast of the HSQ only a 22 nm wide line reached the optimum exposure dose. The size and shape measurement of the proton beam at the nanometer range is clearly a problem in finding the optimum performance of HSQ under proton beam exposure. Measurement of these beam parameters will be improved in the future with the use of a more accurate resolution standard fabricated with a side wall slope of about 14 nm.[22]

In the last experiment a grating was written in the 100 nm HSQ layer in an area of 25 × 50 μm^2. The repeat distance was chosen to be 300 nm. Here a fluence of 1.9 × 10^6 protons per μm^2 was used to expose the grating. This exposure resulted in a regular grating with 68 nm lines and 230 nm spaces; see Figure 4. This is a test structure for future applications in the production of optical components. In this experiment the HSQ samples were exposed and developed

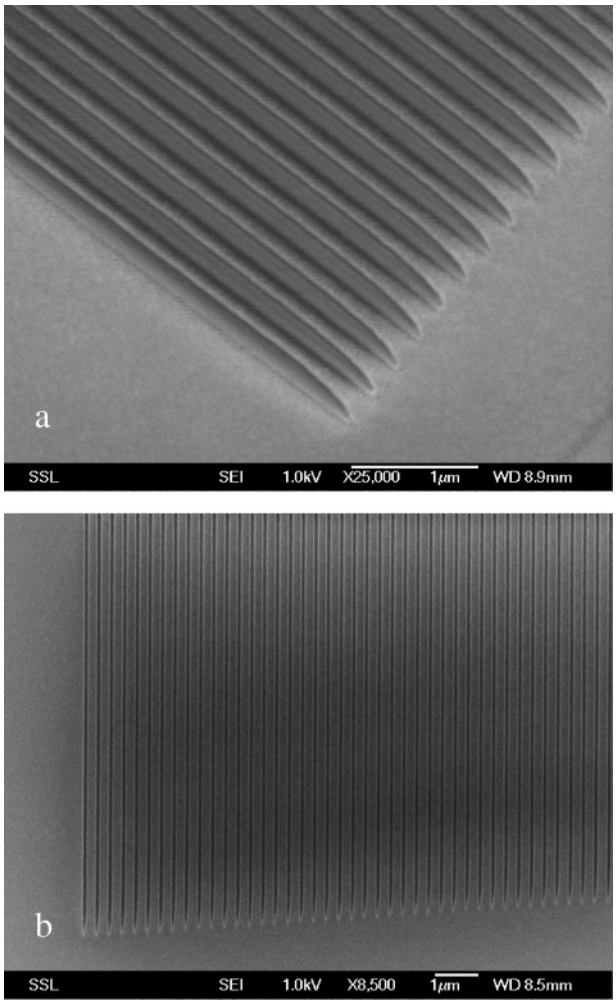

Figure 4. SEM images of a grating in 100 nm thick HSQ exposed with a 2 MeV H_2^+ beam in an area of 25 × 50 μm^2.

after 2 days. In a follow-up experiment a postexposure delay of 17 days was applied. In this subsequent experiment the lines and spaces were not separated and a uniform area of HSQ (25 × 50 μm^2) was obtained after development. This shows that postexposure delay leads to undesirable deterioration in resolution and should be avoided. Similar problems have been reported for e-beam exposure of HSQ.[7]

In summary, these results in HSQ show the great potential of p-beam writing for 3D nanolithography. The performance of p-beam writing is dependent on how well we can focus megaelectronvolt protons, and here we show through the HSQ written nanowalls that we can achieve details down to the 20 nm level. Proton beam technology development is still in its infancy, and there is no scientific reason this performance should not be improved. Further, due to the reduced proximity effects compared with the highly successful e-beam writing, p-beam writing offers a novel way of producing 3D high-spatial-density nanostructures.

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