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Adhesion of proton beam written high aspect ratio hydrogen silsesquioxane (HSQ) nanostructures on different metallic substrates

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ABSTRACT

Hydrogen silsesquioxane (HSQ) behaves as a negative resist under MeV proton beam exposure. HSQ is a high-resolution resist suitable for production of tall (<1.5 μm) high aspect ratio nanostructures with dimensions down to 22 nm. High aspect ratio HSQ structures can be used in many applications, e.g. nanofluidics, biomedical research, etc. Isolated HSQ nanostructures, however, tend to detach from substrates during the development process due to the weak adhesive forces between the resist and the substrate material. Larger proton fluences were observed to promote the adhesion. To determine an optimal substrate material and the proton irradiation doses for HSQ structures, a series of 2 μm long and 60–600 nm wide free-standing lines were written with varying fluences of 2 MeV protons in 1.2 μm thick HSQ resist spun on Ti/Si, Cr/Si and Au/Cr/Si substrates. The results indicate that the Ti/Si substrate is superior in terms of adhesion, while Au/Si is the worst. Cr/Si is not suitable as a substrate for HSQ resist because debris was formed around the structures, presumably due to a chemical reaction between the resist and Cr.

1. Introduction

Hydrogen silsesquioxane (HSQ) is an inorganic polymer material which acts as a high-resolution negative tone resist [1,2]. High-spatial-density lines with widths below 20 nm [3] and single lines down to 6 nm [4] have been resolved in HSQ using e-beam writing and 26 nm resolution for EUV lithography has been reported [5]. Due to the high contrast properties of HSQ (0.55–3.2 for e-beam writing [3,6,4]) and its excellent mechanical properties, nanostructures with aspect ratios up to 10 can be produced even using 50 keV e-beam lithography [7]. By increasing the electron energy to 100 keV an aspect ratio of 13 was achieved [8]. HSQ nanostructures with higher aspect ratio tend to collapse after the development process during resist drying. Using supercritical resist drying with CO_2 instead of conventional resist drying by nitrogen (N_2) blow has been shown to be suitable for production of high density lines with an aspect ratio of about 20 [9]. Recently, it has been shown that HSQ can also be used as a proton beam writing (P-beam writing) resist. P-beam writing has been developed at the Centre for Ion Beam Applications in the Physics Department of the National University of Singapore [10]. This technique in its principle is similar to e-beam lithography. A beam of MeV protons from an accelerator is focused into a small beam spot which is magnetically scanned over the resist surface to generate a latent image of the desired pattern. The advantage of MeV protons, as opposed to keV electrons, is that MeV protons can penetrate deep into the resist along a straight path with minimal scattering. In p-beam writing, as well as in e-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, the secondary electrons produced by the MeV protons have low energies. The primary delta-electrons have energies extending from zero for the electrons scattered perpendicularly to the proton trajectory to a maximum of 4 keV (for 2 MeV protons) for the head-on proton–electron collisions. However, since the cross-section for a head-on collision is extremely small, most of the delta-electrons have low energies (typically less than 100 eV [11,12]). This results in sharp localization of the deposited energy within just a few nm around the proton track where 90% of the electron energy is deposited [13], thereby sharply reducing the

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level of proximity exposure [12,14]. The technique is thus suitable for production of high-spatial-density and high aspect ratio structures. Using p-beam writing, 22 nm lines in 850 nm thick HSQ have been demonstrated [15,16]. The lines have an aspect ratio of 39, and when the proton fluence is increased, they are sufficiently rigid to remain standing even without the use of supercritical drying which is necessary for successful development of e-beam written HSQ structures. Unfortunately, high aspect ratio HSQ nanostructures are easily peeled from the substrates during the pattern development process [7] due to the insufficiently strong adhesive forces. In this study, we have investigated the adhesion of proton beam written HSQ structures to metallic substrates. Three different substrates were tested in this study: Ti/Si, Cr/Si and Au/Cr/Si. The latter is widely used as a seed-layer when Ni electroplating is going to be performed after pattern development. Ti/TiO and Cr/Cr_2O_3 are often used as adhesion promoters due to their high surface energy.

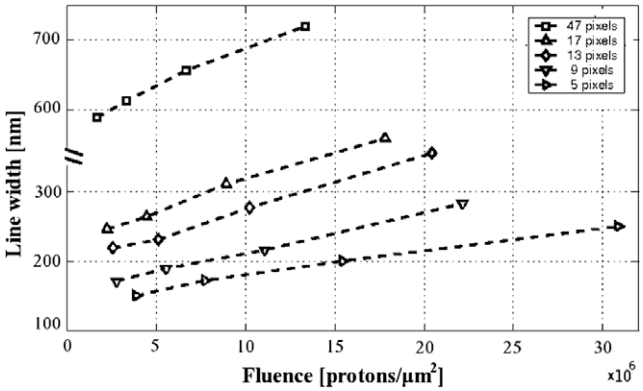

Fig. 1. Measured widths of different lines written with 2 MeV protons in 1.2 μm thick HSQ on Cr/Si, Ti/Si and Au/Cr/Si substrates as function of the proton fluence.

2. Experimental

Clean Si substrates were coated with 10 nm thick Ti and Cr films by Filtered Cathodic Vacuum Arc and Ar sputtering deposition, respectively. Prior to the sputter deposition of 10 nm thick Au films, the Si substrates were sputter-coated with 2–3 nm Cr films to ensure good adhesion. All the samples were then coated with a 1.2 μm thick layer of HSQ (FOx-17, Dow Corning) by spin-coating for 30 s at 3000 rpm. The samples were subsequently prebaked for 120 s at 150 °C. The proton beam writing facility at the Centre for Ion Beam Applications, National University of Singapore [10,17–22], was used to expose patterns in HSQ. The patterns which were made up of individual lines of various width were written in HSQ using a focused beam of 2 MeV protons. The lines were digitized using 4096 × 4096 pixels in a writing field of 50 × 50 μm^2, where each line was 5–47 pixels wide (corresponding to 60–570 nm) and 150 pixels long (1.8 μm). The gap between the lines is about 10 μm in both *x* and *y* directions. The lines were written with various proton fluences corresponding to 0.8–30 × 10^6 protons over total exposure areas of 0.1–1.05 μm^2. After the exposure the samples were developed in 2.38% tetramethyl ammonium hydroxide (TMAH) solution for 60 s followed by rinsing in DI-water. The samples were left under the clean room fumehood's airflow until completely dry without applying N_2 blow drying to avoid detoriation and detachment of the structures from the substrates.

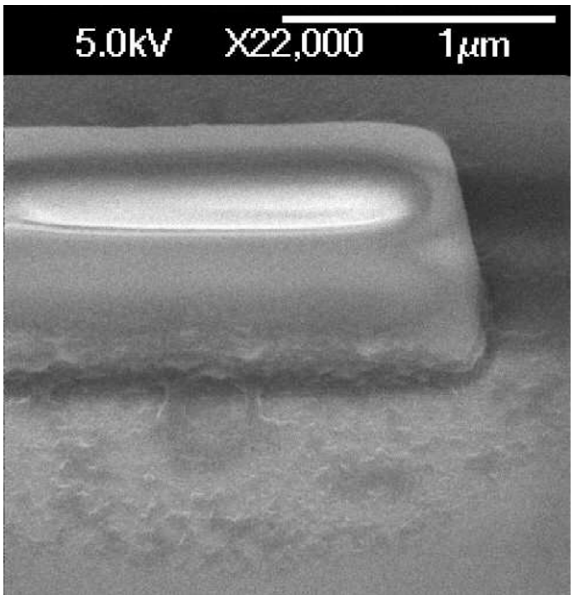

Fig. 2. "Halo"-like grainy structures around lines written on a Cr/Si substrate.

3. Results and discussion

Fig. 1 shows the measured line width versus delivered proton fluence for 5–47 pixels wide lines. In this experiment the size of the focused proton beam was measured to be 90 × 300 nm following the procedure described in [24,25]. A broadening of the line width is observed as the proton fluence is increased. This broadening is caused not by the proximity effects but rather by the Gaussian lateral beam current density profile – as the fluence is increased, wider areas reach the optimum exposure dose. The lines are narrower than the intended exposure patterns. This discrepancy between the size of the exposed pattern and the measured HSQ line width is discussed in more detail by van Kan et al. [15]. Around the lines on the Cr and Ti substrates (Fig. 2) "halo"-like rough grain-structures were observed. The halo size weakly depends on the proton fluence delivered to the corresponding line, and slightly broadens and thickens as the proton fluence is increased. No halo is present around the lines written on the Au substrates, however, no 5–13 pixels wide exposed lines were found. These were believed to be washed away from the substrate during the development due to the poor adhesion of individual HSQ lines to Au. The 47-pixels wide lines written as a reference start to appear on Au only after the fluence reaches 17.8 × 10^6 protons μm^{-2}. At this fluence only a few 17-pixels wide lines can be observed, and a fluence as high as 34 × 10^6 protons μm^{-2} is required to ensure good adhesion of these lines to Au. It is assumed that the adhesion forces increase with the increase of the total contact surface of an individual HSQ line on Au due to the line width broadening at increased fluences. On Ti and Cr substrates even the 5-pixels wide lines written with a fluence of 3.8 × 10^6 protons μm^{-2} were well resolved.

The size of the "halo" observed around the lines on the Ti and Cr substrates is larger than the originally exposed areas. This increase is probably produced by protons from the Gaussian tail of the focused beam and those scattered from the beam-defining object-slit edges. These scattered protons have reduced energies and generally are filtered out by the magnetic fields of the beam switching magnet and the quadrupole triplet focusing lenses. Those protons which lose only a small fraction of their energy during their passage through the slit edges [23] and protons that lose some of their energy in the collisions with the residual gas molecules in the beamline, are likely to be diverted by the focusing magnets into the region around the well-focused Gaussian proton beam spot. The intensity of the halo around the focused beam spot is rather

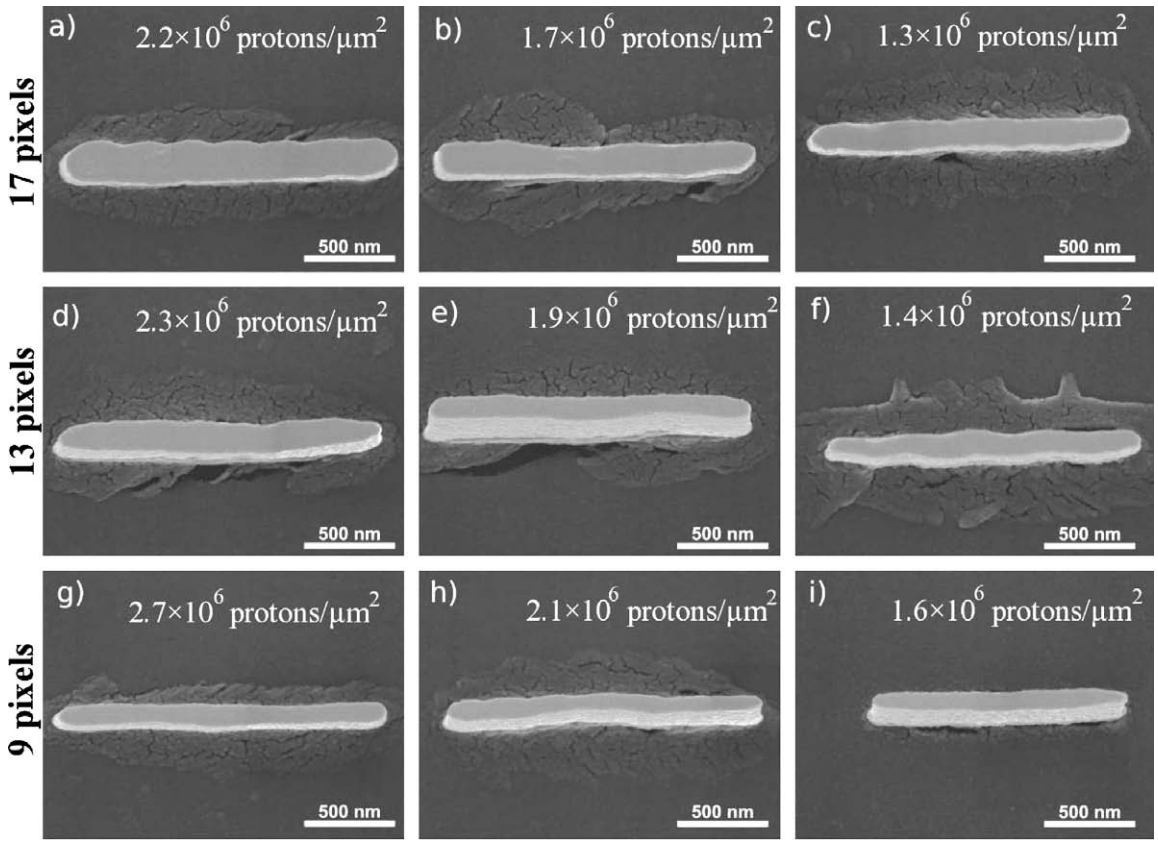

Fig. 3. Lines of different width written with 2 MeV protons in 1.2 μm thick HSQ on a Cr/Si substrate.

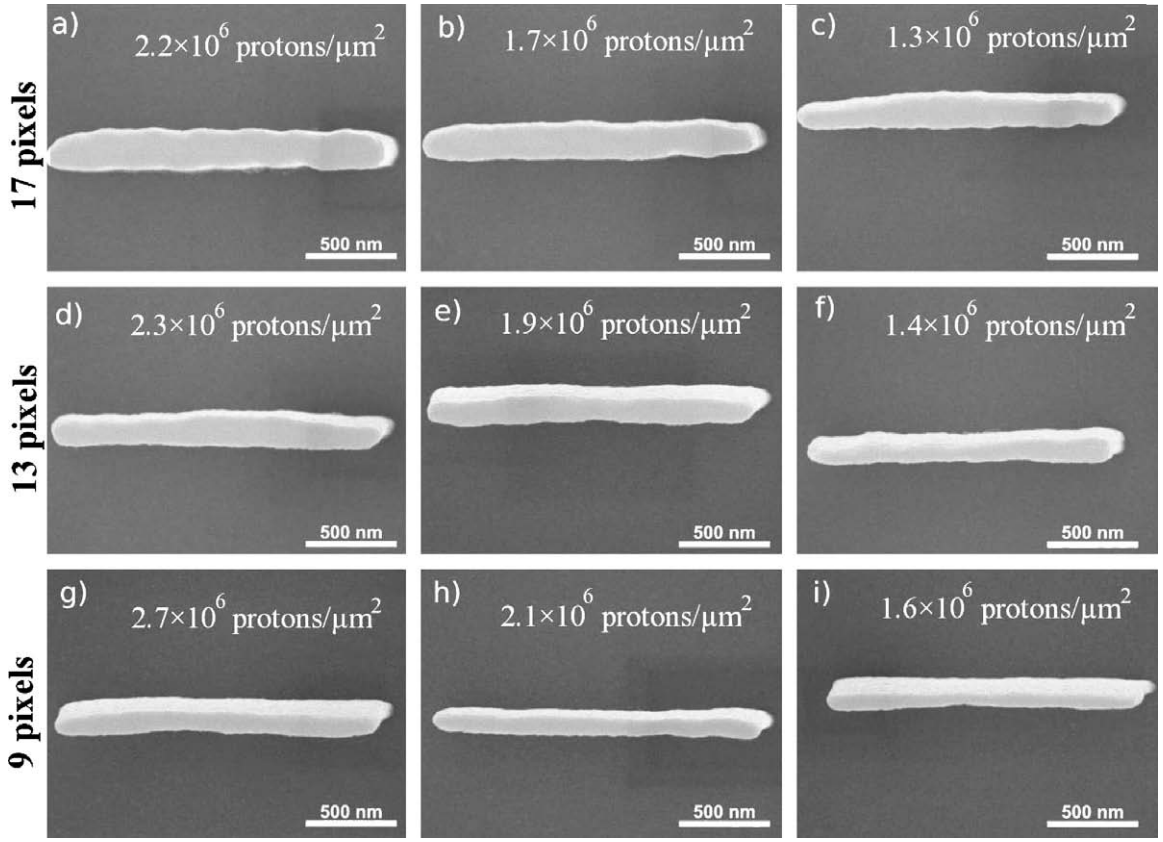

Fig. 4. Lines of different width written with 2 MeV protons in 1.2 μm thick HSQ on a Ti/Si substrate.

small and generally has little or no effect when conventional resists, e.g. PMMA and SU-8, are used.

In the next experiment, to reduce the intensity of the beam halo around the focused beam spot, the beam-defining object-slits were exchanged. In addition, some lines were written with reduced fluences to investigate the adhesion dependence on fluence. In this experiment, the beam was focused down to 90×170 nm^2 spot size [24,25]. In Figs. 3 and 4 SEM micrographs of individual various width HSQ lines on Cr and Ti substrates written with different protons fluences are depicted. The edge waviness of the lines is on the order of 10–20 nm and attributed to the proton beam current fluctuations (5–10%). The lines that were written with a low proton fluence (<1.3–1.6 $\times 10^6$ protons μm^{-2}) are not sufficiently rigid and collapse due to the insufficient crosslinking of the resist and the action of the capillary forces during the development process of the high aspect ratio lines (9-pixels wide line written with a 1.6×10^6 protons μm^{-2} fluence has a width of 80 nm which corresponds to an aspect ratio of ~15). The collapse probability is related to the line width, the fluence and the substrate (Fig. 5 and Table 1). The "halo" around the lines on the Ti surface is almost absent, but starts to appear when the proton fluence exceeds 2.1–2.7×10^6 protons μm^{-2}, however, the extent was much smaller than around the previously written lines due to the better beam spot quality associated with the better edge-quality of the beam-defining slits.

The absence of the "halo" around the lines produced on the Au substrate and smaller extent of the effect on the Ti/Si than on the Cr/Si suggest that the "halo" is caused by a chemical reaction at the interface between the exposed HSQ and the substrate material that is induced by the proton irradiation. It has been previously reported that structural changes and a chemical reaction take place at the interface between HSQ and Ti at elevated temperatures (>400–650 °C [26,27]). Between 550 and 600 °C a considerable loss of H from HSQ occurs, and Ti reacts with HSQ through a mechanism similar to the Ti/SiO_2 system forming Ti_5Si_3 and Ti(O), or with SiH_4, which is a byproduct of HSQ densification, forming Ti–Si. It has been also reported that at elevated temperatures (>400 °C) Si readily diffuses from Si(1 1 1) substrate towards the Cr/Cr_2O_3 film [28]. The Si atoms react with the Cr_2O_3, forming SiO_2 and $CrSi_2$. The elevated temperatures are necessary to break the chemical bonds to make the reactions possible. It has been previously reported that thermal annealing cross-links HSQ via redistribution of the Si–H and Si–O bonds [29,30]. The irradiation of HSQ with keV electrons or MeV protons has a similar effect on the resist and results in broken chemical bonds (Si–H) in HSQ which initiates the cross-linking [1]. The chemical reaction at the HSQ/Cr and HSQ/Ti interfaces is possibly initiated by low energy secondary electrons produced by MeV protons that break chemical bonds making chemical reactions possible.

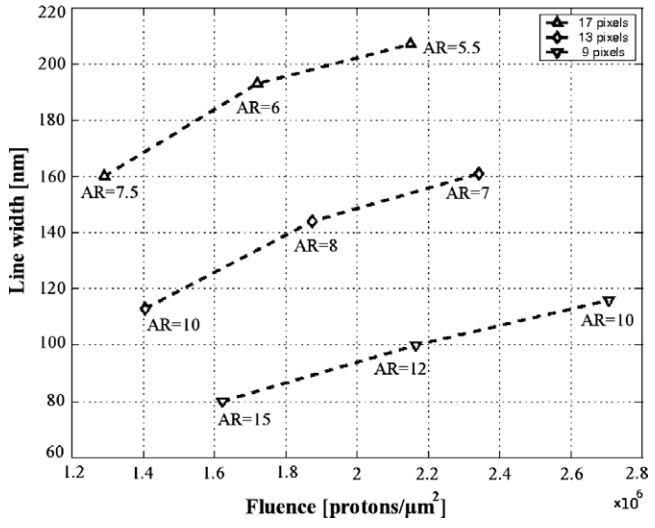

Fig. 5. Measured widths (average) of different lines written with 2 MeV protons in 1.2 μm thick HSQ on Cr/Si and Ti/Si substrates as function of the proton fluence. The aspect ratio (AR) is given for every line.

Table 1
Collapse probability of individual HSQ lines of various width written with different proton fluences on Ti/Si substrate (the values in parentheses correspond to Cr/Si substrate). See also Figs. 3 and 4 for the fluences corresponding to each line. NA (data not available) means that no lines were observed on the samples as the structures were probably washed off the samples during development.

Fluence ($\times 10^6$ protons μm^{-2})	2.2–2.7	1.7–2.1	1.3–1.6	0.9–1.1
17-Pixels	0(0)	0(0)	0(0)	0.35(0.8)
13-Pixels	0(0)	0(0)	0(0.15)	0.75(0.9)
9-Pixels	0(0)	0(0)	0.3(0.5)	1(NA)
5-Pixels	0.1(0.25)	0.95(1)	1(NA)	NA(NA)

4. Conclusion

Test patterns made of individual lines of various width were written with 2 MeV protons in HSQ spun on Cr/Si, Ti/Si and Au/Cr/Si substrates. No structures with an aspect ratio >2 were found on Au/Cr/Si as they were peeled off from the substrate during the development due to the weak adhesion of the HSQ to Au. Lines with an aspect ratio above 15 were resolved on Cr/Si and Ti/Si. The adhesion to Ti/Si was found to be superior to that on the Cr/Si substrate. A rough grain-like "halo" was found around the lines on Cr/Si and to a lower extent on Ti/Si. Presumably, a chemical reaction induced by the proton irradiation takes place at the interface between HSQ with Ti and Cr. The size and thickness of the "halo" depends on the delivered proton fluence per line.

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