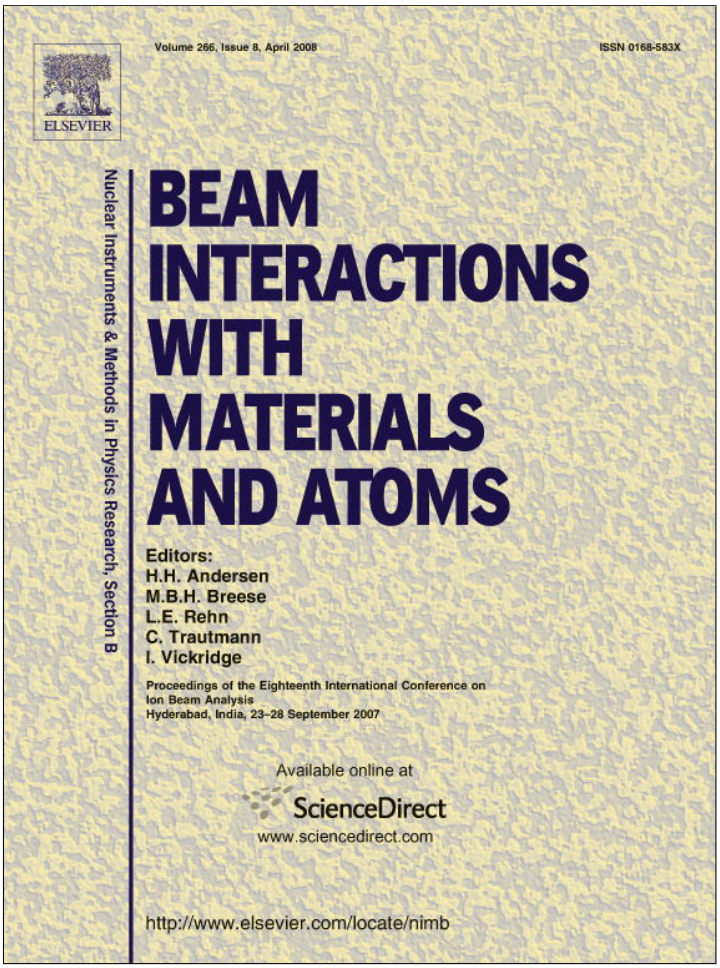

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Exposure parameters in proton beam writing for hydrogen silsesquioxane

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Abstract

In proton beam writing (PBW) a focused MeV proton beam is scanned in a predetermined pattern over a resist (e.g. PMMA, SU-8 or HSQ), which is subsequently chemically developed. 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 the secondary electrons induced by the primary proton beam have low energy and therefore a limited range, resulting in minimal proximity effects. The low proximity effects exhibited by p-beam writing coupled with the straight trajectory and high penetration of the proton beam enables the production of high aspect ratio, high density 3D micro and nanostructures with well defined smooth side walls to be directly written into resist materials. This property together with the stability and focusing power of the end station ensures even exposures with nm smoothness and allows fabrication of details down to the 20 nm level. In this paper, we present results like contrast and sensitivity for PBW using, hydrogen silsesquioxane (HSQ) and XR-1541, both are non-C based resists. Unlike PMMA and SU-8 resist HSQ shows aging effects, requiring optimized processing parameters in PBW.

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Keywords: Proton beam writing; Direct write; High aspect ratio; Nanolithography

1. Introduction

Hydrogen silsesquioxane $(HSiO_{3/2})_8$ (HSQ) and XR-1541 from Dow Corning are well known high resolution negative tone electron beam (e-beam) resists [1,2]. Details down to 7 nm [3,4] and resolutions below 20 nm have been reported [5]. Typical contrast reported for HSQ ranges from 0.55 up to 3.2 for e-beam writing [5–7]. HSQ can also be used as an extreme ultraviolet (EUV) resist using 13.4 nm wavelengths [8], and high density 26 nm wide lines have been demonstrated. For EUV a contrast of 1.64 has been reported [8]. Low energy He^+ ions (75 keV) have also been used, although the imaging properties of these low energy ions have not been reported [9]. For e-beam writing it has been demonstrated that HSQ has a limited functional lifetime, i.e. the contrast degrades as the resist ages [6].

In nanolithography it is extremely important to know how particles or light interact with the resist. This knowledge will enable the accurate planning of resist exposure. The slowing-down and ensuing energy deposition of energetic charged particles (e.g. MeV 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 proton beam writing (PBW), the energy loss of the primary beam is dominated by energy transfer to substrate electrons.

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Unlike the high energy secondary electrons generated during e-beam writing, secondary electrons induced by the primary proton beam have low energy [10,11] (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 crosslinking 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 increased ability to break the Si–O bonds [9]. In PBW 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 cage-like HSQ structure is broken and a network is formed through crosslinking via similar mechanisms to those observed in e-beam writing and EUV irradiation of HSQ.

The low proximity effects exhibited by MeV protons coupled with the straight trajectory and high penetration of the proton beam in resist material enables the fabrication of high density 3D micro and nanostructures with well defined smooth side walls [12], these characteristics are of vital importance for the fabrication of optical components and LIGA X-ray masks [13–16]. No proximity effects have been observed so far in preliminary PBW experiments [17]. Up to now the only resists compatible with PBW which have demonstrated sub-100 nm features are PMMA, SU-8 and HSQ. Other resists like PMGI [18], Diaplate 133 [19] and a resist based on epoxy and polyhydroxystyrene (TADEP) polymers [20] have been investigated for their effectiveness in combination with PBW, but so far none of these resists have exhibited sub-100 nm resolution [21]. In the case of TADEP 100 nm details have been achieved recently [22].

PBW in combination with PDMS casting shows great potential [23–25], since HSQ has shown superior feature details in PBW [26,27], it is a natural candidate as a mold for PDMS casting. Writing masters in HSQ resulted in non-reproducible results due to sensitivity variation in different batches of HSQ. Therefore it is crucial to better understand the effect of MeV protons on the extent of crosslinking for different batches of HSQ and XR-1541 resist. In order to optimize the fabrication of 3D nanostructures in HSQ we studied the sensitivity and contrast of different batches of HSQ and XR-1541 using MeV protons.

2. Experimental procedures

2.1. Hardware set-up

PBW has been developed at the Centre for Ion Beam Applications (CIBA) in the Physics Department of the National University of Singapore [17,28]. This technique employs a focused MeV proton beam scanned in a predetermined pattern over a suitable resist (e.g. PMMA, SU-8 or HSQ) which is subsequently chemically developed. Further details of the PBW set-up can be found in [29].

2.2. Experimental procedure and results

In this study with PBW on HSQ, six Si wafers coated at various thicknesses are evaluated. In all cases a Si wafer was pre-coated with Cr and Au to promote adhesion of HSQ and improve delamination characteristics of PDMS after PDMS casting, required in follow-up experiments. Not all the thicknesses could be obtained directly therefore for wafers 2–4 the HSQ was diluted in methylisobutylketone (MIBK) prior to spin coating. A summary of the details and characteristics of the six different wafers are listed in Table 1.

All wafers were pre-baked for 120 s at 150 °C after spin coating and were exposed in September 2007. After the exposure the samples were developed in a 2.38% tetramethyl ammonium hydroxide (TMAH) solution for 60 s followed by a DI water rinse. To measure the contrast curves for the different wafers squares of $5 \times 5\ \mu m^2$ were written with a focused 2 MeV proton beam. The dose was varied from 10 to 500 nC/mm^2 for all the six wafers. In Fig. 1(a) the squares obtained for the first wafer (850 nm thick, coated in March 2005) are shown ranging from 10 to 50 nC/mm^2. The resist already starts to crosslink at 10 nC/mm^2. In Fig. 1(b) wafer 3 shows that the resist becomes hard at a dose of 40 nC/mm^2. In Fig. 1(c) results obtained with wafer 6 are shown. Here the resist starts to crosslink at a dose of 100 nC/mm^2. Note that two squares were written with 100 nC/mm^2 but only one was crosslinked enough to survive the development procedure, this is most likely caused by beam intensity variation (5–10%) and the high contrast.

The thickness of the squares in the six samples was determined with atomic force microscopy (AFM) in

Table 1
Processing parameters and characteristics for the HSQ coated Si wafers

Wafer	Thickness (nm)	Resist	Shipment date	Coating date	Contrast $1/[\log(D_f) - \log(D_i)]$	Sensitivity (nC/mm^2)
1	850	Fox-17	09-03-2005	18-03-2005	1.2 +/− 0.2	32 +/− 3
2	310	Fox-17 diluted (2:3)	09-03-2005	03-10-2005	1.4 +/− 0.2	53 +/− 5
3	120	Fox-17 diluted (1:5)	09-03-2005	10-09-2007	2.2 +/− 0.2	95 +/− 10
4	130	Fox-17 diluted (1:4.2)	31-05-2006	25-07-2007	8 +/− 1.0	200 +/− 40
5	320	Fox-13	31-05-2006	19-09-2006	10 +/− 1.0	150 +/− 30
6	60	XR-1541	16-10-2006	25-07-2007	7.5 +/− 0.5	120 +/− 10

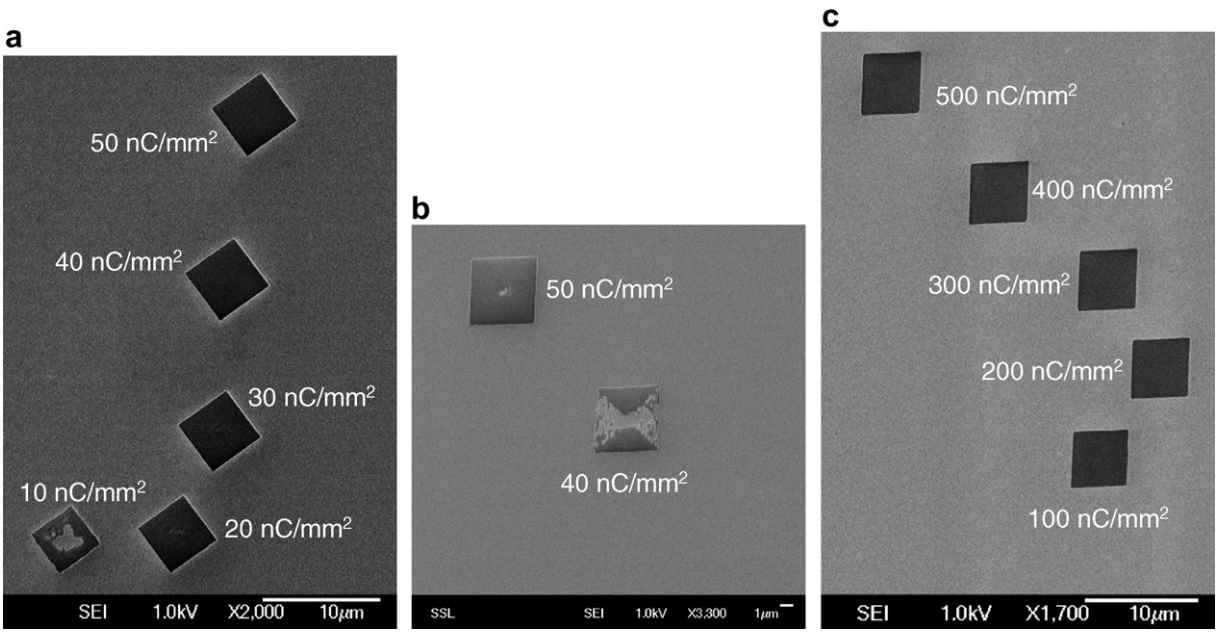

Fig. 1. SEM images of 5×5 μm^2 squares written with a 2 MeV proton beam: (a) exposed in wafer 1 with 10–50 nC/mm^2, (b) exposed in wafer 3 with 40 and 50 nC/mm^2 and (c) exposed in wafer 6 with 100–500 nC/mm^2.

tapping mode. To compare the different wafers directly, all the thicknesses were normalized to 1. Here the normalized thickness is the thickness at which the resist is fully crosslinked. The contrast curves for wafers 1, 2, 3 and 6 are shown in Fig. 2. The wafers 4 and 5 show similar behavior as wafer 6.

To evaluate the different wafers the contrast is calculated, 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 for the developer. In earlier experiments the contrast for wafer 1 was measured to be 3.2 directly after shipment [26] and 1.7 after 275 days [27]. In the current measurements the contrast for wafer 1 has dropped to 1.2, indicating the resist has deteriorated. In Table 1 contrast values for all the 6 wafers are given. Similar contrast values have been reported for e-beam writing in HSQ [6,7]. Freshly coated wafer 3 has a contrast of 2.2, comparing this with the values found for wafers 1 and 2 it can be concluded that

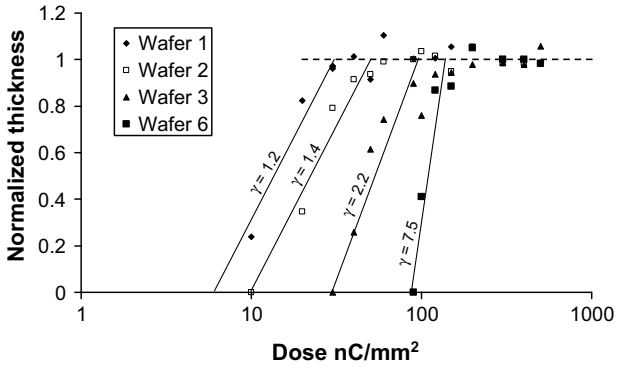

Fig. 2. Contrast curve for wafers 1, 2, 3 and 6 for 2 MeV proton exposure. The thickness is normalized to one, for fully crosslinked resist.

it is best to coat the wafers directly before proton exposure. It was reported that the sensitivity and contrast of HSQ also changes as a function of delay between the different process steps in e-beam writing [6].

We define the sensitivity as the point where the layer is fully insoluble and reaches the maximum thickness, and for wafer 1 we have measured a sensitivity of 32 nC/mm^2. The sensitivities for all the six wafers are listed in Table 1. Comparing the contrast of wafer 1 (Fox-17 obtained in 2005) with the later batches of HSQ and XR-1541, it is observed that about 5 times more protons are required for the same level of crosslinking. At the same time it is observed that the contrast in the new batches has gone up by a factor of 2.5.

In a subsequent experiment, sets of parallel lines were written with a focused 2 MeV proton beam in wafer 1. The lines were digitized using 4096×4096 pixels in a writing field of 40×40 μm^2, where each line is 2 pixels wide. Here a 2 MeV proton beam was focused down to a spot size of 100×200 nm^2. The developed lines are between 50 and 150 nm wide depending on the proton fluence used, see Fig. 3. The lines were fabricated with a fluence of 4.7×10^6 up to 6.3×10^7 protons in an exposure pattern of 1 μm^2. This corresponds to a maximum aspect ratio of 17. Despite aging of the HSQ resist it is still possible to write 30 nm wide lines, written in wafer 3, not shown here.

3. Summary

In summary, these results in HSQ show the potential of PBW for 3D nanolithography. The draw back in using HSQ is the variation in contrast and sensitivity. The HSQ resist has a limited shelf life which makes timing in HSQ resist processing a critical factor in achieving nm sized

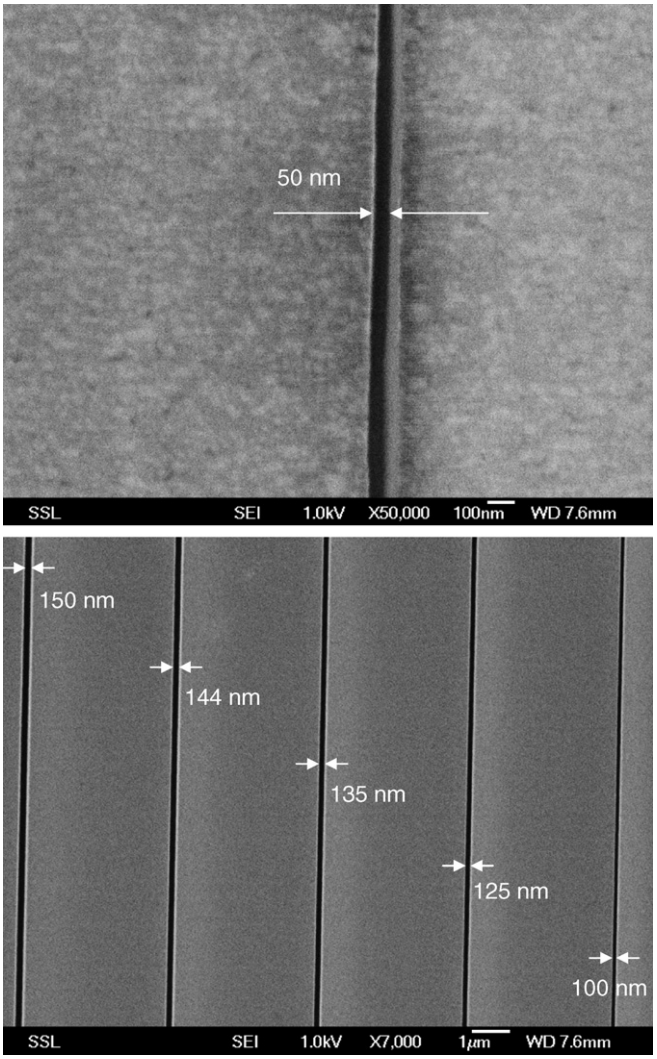

Fig. 3. SEM images of narrow lines exposed in wafer 1 (coated in 2005 and exposed in 2007), featuring 150 down to 50 nm wide lines exposed with 2 MeV protons in 850 nm thick HSQ resist.

high aspect ratio features. Structuring of ultimate feature sizes requires short delay times between spin coating and proton beam exposure. The data provided in this paper can serve as a guide line for obtaining nm sized features in HSQ resist in PBW experiments. Proton beam technology development is still in its infancy, and there is no scientific reason why this performance should not be improved. Further, due to the reduced proximity effects compared with the highly successful e-beam writing, PBW offers a novel way of producing 3D high density nanostructures.

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