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ScienceDirect
Nuclear Instruments and Methods in Physics Research B 260 (2007) 396–399
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Hydrogen silsesquioxane a next generation resist for proton beam writing at the 20 nm level

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Available online 14 February 2007

Abstract

In proton beam writing (PBW) the only compatible resists which have demonstrated sub-100 nm features are PMMA and SU-8. In this paper, we present results on PBW using a new non C based, hydrogen silsesquioxane (HSQ) resist. The results obtained with PBW using the HSQ resist, show that HSQ behaves as a negative resist under proton beam exposure. Details down to the 20 nm level in width standing at a height of 850 nm have been directly written in HSQ. The superior resolution of HSQ shows great potential but unlike PMMA and SU-8 this resist has a limited shelf life. To optimize the usage of this resist contrast curves and sensitivity of HSQ as a function of shelf life will be discussed. The quest for smaller feature sizes is further complicated by the fact that the beam size determination has an error of about 14 nm.

PACS: 07.78.+s; 85.40.Hp; 81.16.Nd; 81.15.Pq

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

1. Introduction

Hydrogen silsesquioxane $(HSiO_{3/2})_8$ (HSQ), from Dow Corning has been shown to function as a high resolution negative tone electron beam (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 wavelengths [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 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]. For e-beam writing it has been demonstrated that HSQ has a limited functional lifetime, i.e. the contrast degrades as the resist ages [7].

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 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 [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

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doi:10.1016/j.nimb.2007.02.051

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 nano structures with well defined smooth side walls [12]. No proximity effects have been observed so far in preliminary PBW experiments [13]. Up to now the only resists compatible with PBW which have demonstrated sub-100 nm features are PMMA and SU-8. Other resists like PMGI [14], Diaplate 133 [15] and a resist based on epoxy and polyhydroxystyrene polymers [16] have been investigated for their effectiveness in combination with PBW, but so far none of these resists have exhibited sub-100 nm resolution. In this paper, we present results on p-beam writing using HSQ resist down to the 20 nm level which is currently the best performance in PBW. Preliminary findings with PBW in HSQ resist suggest great potential [17,18].

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 [13,19]. 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. 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″. 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. Since a magnetic scanning system has a relatively long settling time resulting in a relative slow writing speed, we have 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 [20], and the ability to stitch fields will be included in the second generation electrostatic scanning system. Further details of the PBW set-up can be found in [21].

2.2. Results

In this study with PBW 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 onto 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 methylisobutylketone (MIBK) (2:3 by volume, respectively) and spin coated for 30 s at 3000 rpm. Both wafers were pre-baked for 120 s at 150 °C after spin coating. After proton exposure the samples were developed in a 2.38% tetramethyl ammonium hydroxide (TMAH) solution for 60 s. The contrast curve for the 850 nm layer was measured and is shown in Fig. 1. Squares of 5×5 μm^2 were written with a focused 2 MeV proton beam, the dose was varied from 10 to 250 nC/mm^2. The proton beam writing was performed 3 days after the spincoating. 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 [14]. This definition for sensitivity is used since a lower exposure dose was found to result in weaker HSQ structures. In a further experiment the HSQ was exposed 275 days after spin coating, here a contrast of 1.7 was found, see Fig. 1. This shows timing is critical in processing HSQ resist in PBW experiments. 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 [7].

In a subsequent experiment, sets of two parallel lines were written with a focused 2 MeV H_2^+ beam using a similar exposure pattern; one set is connected to two supporting structures and the second set consists of free standing lines, both sets are 850 nm high. The lines were digitized using 4096×4096 pixels in a writing field of 100×100 μm^2, where each line is 9 pixels wide (corresponding to 220 nm). The developed lines are 60 nm wide, less than half the width of the exposure pattern, see Fig. 2(a). These

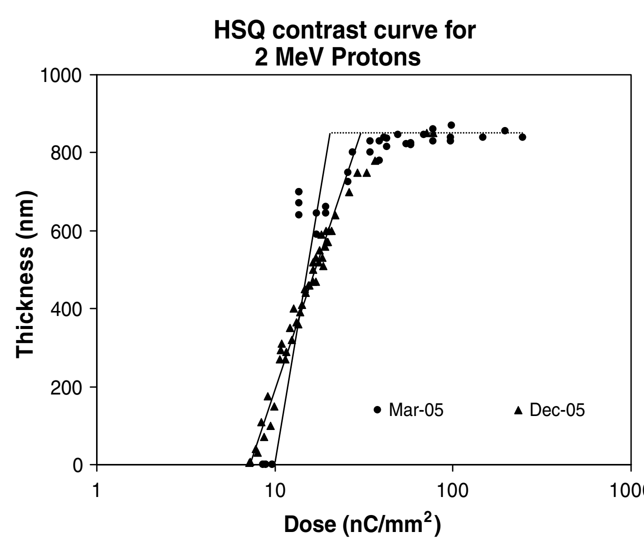

Fig. 1. Contrast curve for 850 nm thick HSQ, exposed to 2 MeV protons, the straight lines correspond to a contrast of 3.2 and 1.7 for the fresh and 10 month old resist, respectively.

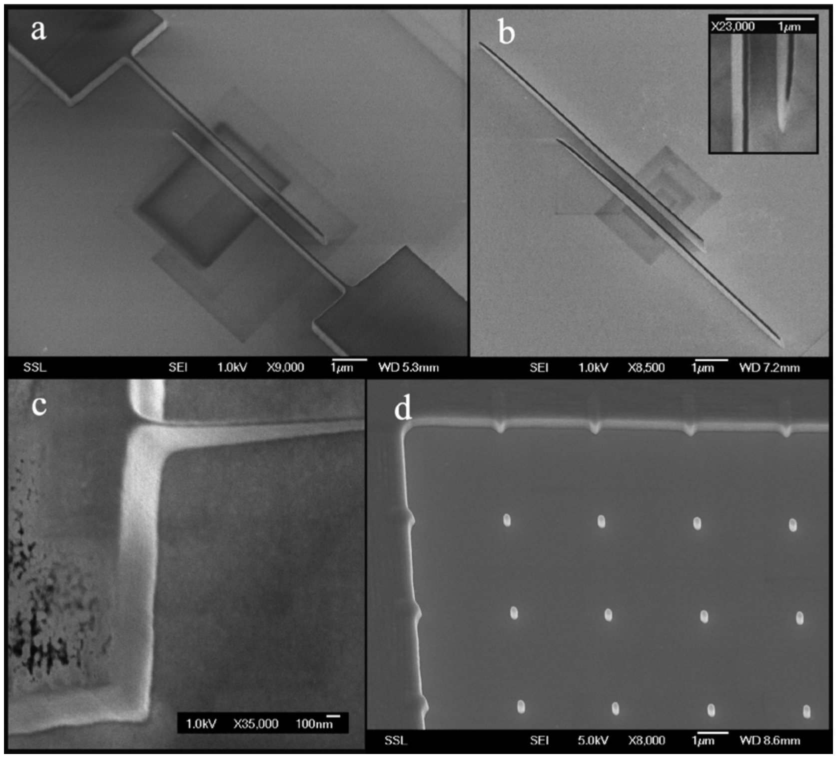

Fig. 2. SEM images of parallel lines written with a 2 MeV H_2^+ beam using a 9 pixel wide exposure pattern in (a) 850 nm thick HSQ with 2.4×10^6 protons and (b) 2.0×10^6 protons in a 7 pixel wide exposure pattern, demonstrating 40 nm wide free standing lines. In (c) 1.2×10^6 protons are used in a 3 pixel wide exposure pattern, demonstrating 22 nm wide lines. SEM image (d) of 150 nm diameter pillars, written with 2 MeV protons.

lines have been fabricated with a corresponding fluence of 2.4×10^6 protons over a total exposure area of 4.3 μm^2. This design, where the lines are connected to the supporting contacts, will be used in future experiments to make electrical contacts for lab on a chip applications. In the second set of lines we can see the strength of HSQ, two 40 nm wide freestanding lines were successfully exposed and developed even without the supporting contacts, see Fig. 2(b). Here a 7 pixel wide line pattern was used, administering a fluence of 2.0×10^6 protons over a total exposure area of 3.3 μm^2. Even smaller structures in HSQ were achieved with PBW: Wall structures were written in a similar way as the previous example except that the number of pixels were reduced to 3 per line in the exposure pattern (1.4 μm^2), see Fig. 2(c). 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 super-critical drying necessary for successful development of e-beam written HSQ structures [5].

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. [21]. 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 [22]. In order 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 centre, 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 nm 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 [23]. More details about the optimized fabrication of this new resolution standard is discussed by Zhang et al. [24].

In a further experiment, sets of orthogonal lines were written with a low dose. The number of protons was lowered to find the point where only at the crossings of the lines enough energy was deposited to crosslink the HSQ. This pattern resulted in a set of nano pillars of 150 nm diameter, see Fig. 2(d). Here 2 MeV protons were used to expose the HSQ.

In the final experiment a grating was written in the 100 nm thick HSQ layer in an area of 25×50 μm^2. The repeat distance was chosen to be 300 nm. Here a fluence of 0.9×10^6 protons per μm^2, was used to expose the

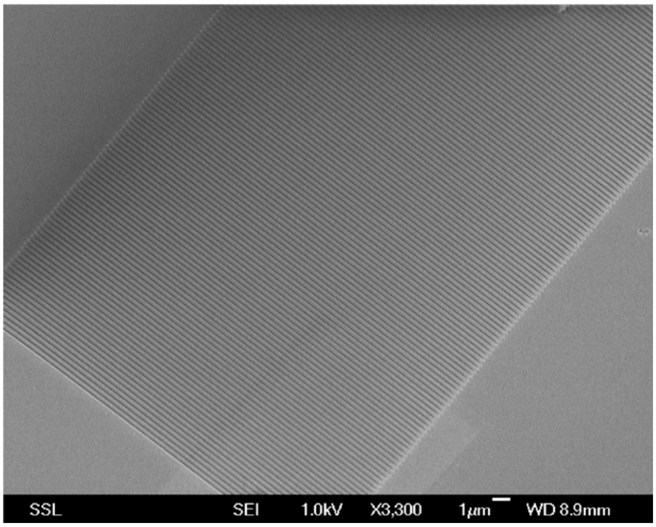

Fig. 3. SEM images of a grating in 100 nm thick HSQ exposed with a 2 MeV H_2^+ beam in an area of 25×50 μm^2.

grating. This exposure resulted in a regular grating with 83 nm lines and 220 nm spaces, see Fig. 3. This is a test structure for future applications in the production of optical components.

3. Summary

In summary, these results in HSQ show the great potential of PBW for 3D nanolithography. The performance of PBW is dependent on how well we can focus MeV protons, and here we show through the HSQ written nano walls that we can achieve details down to the 20 nm level. The HSQ resist has a limited shelf life which makes timing in HSQ resist processing a critical factor in achieving nm sized features. 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.

Acknowledgements

We acknowledge the financial support from ASTAR (Singapore) and the MOE Academic Research Fund as well as the AOARD (Asian Office of Aerospace Research and Development). We also acknowledge Dow Corning for the HSQ test sample.

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