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Proton beam written hydrogen silsesquioxane (HSQ) nanostructures for Nickel electroplating

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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 are required in many applications, e.g. nanofluidics, biomedical research, etc. Since P-beam writing is a direct and hence slow process, it is beneficiary to fabricate a reverse image of the patterns in a metallic stamp, e.g. by Ni electroplating. The Ni stamp can then be used to produce multiple copies of the same pattern. In this study we investigate the possibility to produce Ni stamps from p-beam written HSQ samples. HSQ high aspect ratio nanostructures, however, tend to detach from Au/Si substrates (typically used in electroplating) during the development process due to the weak adhesive forces between the resist and the substrate material. 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 doses 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 both Ti/Si and Cr/Si substrates are superior in terms of adhesion. The adhesion of high aspect ratio HSQ nanostructures to Au/Cr/Si is poor with a maximum aspect ratio of the adhering structures not exceeding two. Cr/Si is not suitable as a substrate for HSQ resist as debris is formed around the structures, presumably due to a chemical reaction between the resist and Cr.

1. Introduction

Hydrogen silsequioxane (HSQ) is an inorganic polymer material which acts as a high resolution negative tone resist [1,2]. High 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 HSQ's high contrast properties (0.55–3.2 for e-beam writing [3,4,6]) and its excellent mechanical properties nanostructures with aspect ratios up to 10 can be produced even with 50 keV e-beam lithography [7]. 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 [8]. 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 and with minimal scattering. The technique is thus suitable for production of high-spatial-density and high aspect ratio structures. Using p-beam writing individual 22 nm lines in 850 nm thick HSQ (aspect ratio of 39) have been demonstrated [9,10].

These high aspect ratio HSQ nanostructures can be used for Ni electroplating to produce a reverse image of the pattern in stamps which can be used to replicate high aspect ratio individual nanostructures in polymers. Such individual structures or arrays of individual structures are required in many applications, e.g. in biomedical research and microfluidics. Using HSQ as a resist for p-beam writing and subsequent electroplating offers a number of advantages compared to another commonly used negative resist, SU-8. As opposed to SU-8, HSQ can be easily removed from the substrate by applying suitable chemicals [11]. Furthermore, HSQ is a high contrast resist suitable for fabrication of sub-50 nm structures [9,10].

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 investigate the adhesion of proton beam written HSQ structures to metallic substrates. Three different substrates

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were tested: Ti/Si, Cr/Si and Au/Cr/Si. The latter is widely used on substrates because of Au's excellent conductivity properties when Ni electroplating is performed after the pattern development. Ti/TiO and Cr/Cr_2O_3 are typically used as adhesion promoters due to their high surface energy.

2. Experimental

Clean Si substrates were coated with 10 nm thick Ti and Cr films by Filtered Cathodic Vacuum Arc and Ar sputtering depositions, respectively. Prior to the sputtering 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 prebaked for 120 s at 150°C after the spin-coating. The proton beam writing facility at the Centre for Ion Beam Applications, National University of Singapore [8,12–17], was used to fabricate individual lines in HSQ. The patterns made 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 $50 \times 50\ \mu m^2$, where each line is 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 $0.8–30 \times 10^6$ protons over total exposure areas of $0.1–1.05\ \mu m^2$. 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. Once dry, some of the samples were characterized with SEM, while others were Ni-electroplated in a commercial plating system from Technotrans AG. Prior to the electroplating, the samples were sputter-coated with a thin Cr/Au layer on top of the resist to form a conductive seed layer. A two-step electroplating process was then employed: firstly, electroplating at small plating rate ($50\ nm\ min^{-1}$) up to a height to cover completely the HSQ structures (∼ 10 μm); secondly, the plating rate was increased ($0.5–1\ \mu m\ min^{-1}$) to create a thick supporting substrate.

3. Results and discussion

Fig. 1 shows individual lines written in HSQ on Cr/Si and Ti/Si substrates. Around the lines"halo"-like rough debris is present. The debris around the lines on the Ti surface is almost absent, but start to appear when the proton fluence exceeds $2.1–2.7 \times 10^6$ protons μm^{-2}, however, at a much lower extent than around the lines on Cr/Si. The debris size weakly depends on the proton fluence delivered to the corresponding line, and broadens and thickens as the proton fluence is increased. No debris are present around the lines written on the Au/Cr/Si substrates, however, no 5–13 pixels wide exposed lines were found, which are believed to be washed away from the substrate during the development because of the poor adhesion of HSQ individual 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 line written with a fluence of 3.8×10^6 protons $\mu\ m^{-2}$ are well resolved (not shown).

The size of the debris observed around the lines on the Cr is a little larger than the originally exposed areas. This increase is probably produced by protons from the Gaussian-like tail of the focused beam and those scattered from the beam defining object slits edges [18]. 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. The protons that lost only a small fraction of their energy during their passage

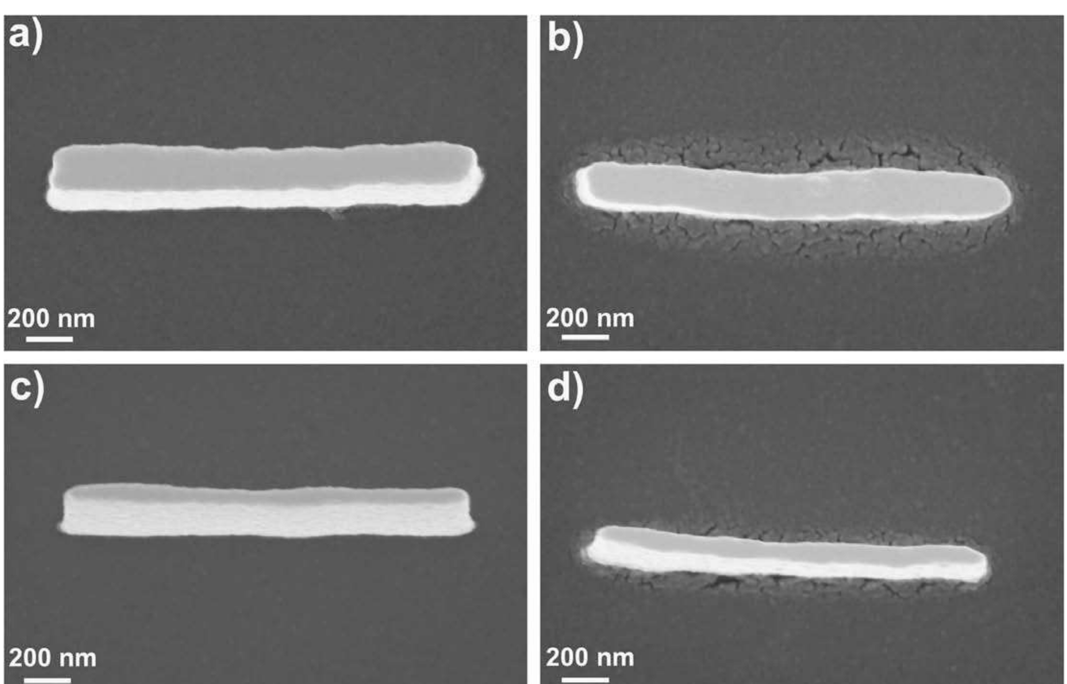

Fig. 1. SEM images of lines written with 2 MeV protons in 1.2 μm thick HSQ on Ti/Si and Cr/Si substrates. (a) and (b) 17-pixels wide line on Ti/Si and Cr/Si written with a 2.2×10^6 protons μm^{-2} fluence, respectively. (c) and (d) 9-pixels wide line on Ti/Si and Cr/Si written with a 2.7×10^6 protons μm^{-2} fluence, respectively.

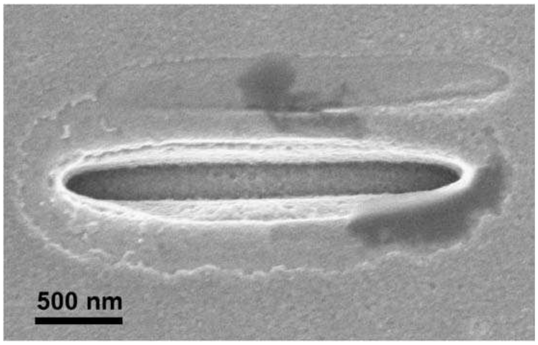

Fig. 2. SEM image of a nanochannel in a Ni stamp fabricated by p-beam writing using HSQ on Ti/Si substrate as a mold.

through the slit edges and those protons that lost 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 small and generally has little or no effect when conventional resists, e.g. PMMA and SU-8, are used.

The absence of the debris around the lines produced on the Au substrate and smaller extent of the effect on the Ti substrate than on the Cr suggest that the debris are caused by a chemical reacton at the interface between the exposed HSQ and the substrate material 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) [19,20]. Between 550–600 °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 [21]. 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 reported that thermal annealing cross-links HSQ via redistribution of the Si–H and Si–O bonds [22,23]. The irradiation of HSQ with keV electrons or MeV protons may have a similar effect on the resist and results in broken chemical bonds (Si–H) in HSQ which initiates the cross-linking [1]. We thus suggest, that the chemical reaction at the HSQ/Cr and HSQ/Ti interfaces is initiated by low energy secondary electrons produced by MeV protons that break chemical bonds making chemical reactions possible.

Fig. 2 shows a nanochannel in a Ni stamp fabricated by Ni electroplating using p-beam written HSQ lines on Tu/Si as a mold. The nanochannels are well resolved, however, the edges of the structures are rough. In addition, the"halo" around the lines is present, which, together with the channels' edge roughness is caused by the debris around the HSQ lines. The debris around the HSQ lines of Ti/Si can be avoided by writing the lines using lower proton fluence ($<2.2–2.7 \times 10^6$ protons μm^{-2}). Such lines are, however, not rigid enough and are either tilted (e.g. Fig. 1c,d) or completely collapse. Naturally, the collapsed or tilted lines cannot be electroplated.

The tilt or collapse of the lines can be prevented by using supercritical resist drying with CO_2 of HSQ instead of conventional resist drying by N_2 blow that follows after-development step and rinsing in water. The supercritical CO_2 drying was shown to be suitable for production of high density and high aspect ratio HSQ nanostructures [24]. The nanochannels in Ni stamps fabricated by using HSQ on Cr/Si mold are significantly deteriorated since the extent and the thickness of the debris around the HSQ lines on Cr/Si is greater than on Ti/Si.

4. Conclusion

Test patterns made of individual lines of various widths 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 substrate was found to be slightly better than to the Cr/Si. Rough grain-like debris is 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 debris depend on the delivered proton fluence per line. Metallic stamps with high aspect ratio features produced by electroplating Ni using HSQ molds were fabricated with limited success as the debris around the structures was reproduced in the stamps.

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References

[1] H. Namatsu, Y. Takahashi, K. Yamazaki, T. Yamaguchi, M. Nagase, K. Kurihara, J. Vac. Sci. Technol. B 16 (1998) 69.
[2] H. Namatsu, T. Yamaguchi, M. Nagase, K. Yamazaki, K. Kurihara, Microelectron. Eng. 41/42 (1998) 331.
[3] F.C.M.J.M. van Delft, J.P. Weterings, A.K. van Langen-Suurling, H. Romijn, J. Vac. Sci. Technol. B 18 (2000) 3419.
[4] M.J. Word. I. Adesida, P.R. Berger, J. Vac. Sci. Technol. B 21 (2003) L12.
[5] I. Junarsa, M.P. Stoykovich, P.F. Nealey, Y. Ma, F. Cerrina, H.H. Solak, J. Vac. Sci. Technol. B 23 (2005) 138.
[6] F.C.M.J.M. van Delft, J. Vac. Sci. Technol. B 20 (2002) 2932.
[7] I.-B. Baek, J.-H. Yang, W.-J. Cho, C.-G. Ahn, K. Im, S. Lee, J. Vac. Sci. Technol. B 23 (2005) 3120.
[8] F. Watt, M.B.H. Breese, A.A. Bettiol, J.A. van Kan, Mater. Today 30 (2007) 20.
[9] J.A. van Kan, A.A. Bettiol, F. Watt, Nano Letters 6 (2006) 579.
[10] J.A. van Kan, A.A. Bettiol, F. Watt, Nucl. Instr. and Meth. B 260 (2007) 398.
[11] F.C.M.J.M. van Delft, F.J.H. van der Kruis, P.P.J. van Eerd, H.A. van Esch, H.W.J.J. van de Laar, J. Vac. Sci. Technol. B 24 (6) (2006) 3125.
[12] J.A. van Kan, J.L. Sanches, T. Osipowicz, F. Watt, Microsyst. Technol. 6 (2000) 82.
[13] J.A. van Kan, A.A. Bettiol, B.S. Wee, T.C. Sum, S.M. Tang, F. Watt, Sensors Actuators A 92 (2001) 370.
[14] J.A. van Kan, A.A. Bettiol, F. Watt, Mat. Res. Soc. Symp. Proc. 777 (2003) T.2.1.1.
[15] J.A. van Kan, A.A. Bettiol, K. Ansari, E.J. Teo, T.C. Sum, F. Watt, Int. J. Nanotechnol. 1 (2004) 464.
[16] A.A. Bettiol, C.N.B. Udalagama, J.A. van Kan, F. Watt, Nucl. Instr. and Meth. B 231 (2005) 400.
[17] J.A. van Kan, A.A. Bettiol, F. Watt, Appl. Phys. Lett. 83 (2003) 1629.
[18] S. Gorelick, H.J. Whitlow, Nucl. Instr. and Meth. B 267/12-13 (2009) 2050.
[19] Y. Zeng, S.W. Russel, A.J. McKerrow, P. Chen, T.L. Alford, Thin Solid Films 360 (2000) 283.
[20] Y. Zeng, S.W. Russel, A.J. McKerrow, L. Chen, T.L. Alford, J. Vac. Sci. Technol. B 18 (2000) 221.
[21] P. Wetzel, C. Pirri, J.C. Peruchetti, D. Bolmont, G. Gewinner, Surf. Sci. 178 (1986) 27.
[22] M.G. Albrecht, C. Blanchette, J. Electrochem. Soc. 145 (1998) 4019.
[23] W.-C. Liu, C.-C. Yang, W.-C. Chen, B.-T. Dai, M.-S. Tsai, J. Non-Crystal. Solids 311 (2002) 233.
[24] T. Wahbrink, D. Küpper, Y.M. Georgiev, J. Bolten, M. Möller, D. Küpper, M.C. Lemme, H. Kurz, Microelectron. Eng. 83 (2006) 1124.