

Orthogonal and fine lithographic structures attained from the next generation proton beam writing facility

Y. Yao, P. Santhana Raman & J. A. van Kan

Microsystem Technologies
Micro- and Nanosystems Information
Storage and Processing Systems

ISSN 0946-7076

Microsyst Technol
DOI 10.1007/s00542-014-2066-2



Your article is protected by copyright and all rights are held exclusively by Springer-Verlag Berlin Heidelberg. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".

Orthogonal and fine lithographic structures attained from the next generation proton beam writing facility

Y. Yao · P. Santhana Raman · J. A. van Kan

Received: 5 June 2013 / Accepted: 2 January 2014
© Springer-Verlag Berlin Heidelberg 2014

Abstract A second generation proton beam writing (PBW) system has been built at the Centre for Ion Beam Applications at the National University of Singapore for fabrication of high aspect ratio 3D nano lithographic structures. System improvements and a few lithographic structures obtained with this facility are presented in this paper. Through accurate alignment of the magnetic quadrupole lenses and the electrostatic scanning system, orthogonal beam scanning has been achieved. The earlier constrain of limited beam scan area has been overcome by adopting a combination of beam and stage scanning as well as stitching. With these improvements smallest ever Ni structure of 65 nm in width has been fabricated using nickel electroplating on a proton beam written PMMA sample in the second generation PBW facility. Using this improved PBW facility, we have also demonstrated the fabrication of fine lithographic patterns with 19 nm line width and 60 nm spacing in 100 nm thick negative high resolution hydrogen silsesquioxane resist. Future possible system improvements leading to finer resolution will be discussed briefly.

1 Introduction

In an era of miniaturization, lithography is a vital tool to fabricate structures in nanometric regime. The limitation of 193 nm diffraction constrain associated with optical lithographic technique has started the quest for next generation lithographic (NGLs) techniques (Rothschild et al. 1992). Proton beam writing (PBW), which utilizes high

energy focused sub-100 nm proton beam to direct write micro or nanostructures on materials (van Kan et al. 2003a, b; Teo et al. 2004), is one among other NGLs like electron beam lithography, focused ion beam lithography and X-ray lithography. The superiority of PBW is its ability to have deeper penetration and travel in an almost straight line except at the end of range, which allows fabricating 3D high aspect ratio structures with vertical, smooth sidewall and low line-edge roughness (van Kan et al. 2007). A further advantage of PBW is that the structures have minimal proximity effect due to the low energy of the proton-induced secondary electrons (van Kan et al. 2004; Udalgama et al. 2009). Because of these unique abilities, PBW has been used in many areas like photonics, micro- or nano-fluidics, nano-imprinting and silicon micromachining (Watt et al. 2007).

At the Centre for Ion Beam Applications (CIBA), in the Department of Physics, National University of Singapore, there exist two proton beam writing lines (Watt et al. 2003; van Kan et al. 2011). In the first generation PBW facility, the proton beam can be focused down to $35 \times 75 \text{ nm}^2$. In earlier experiments 100 nm grooves have been fabricated in the positive PMMA resist (van Kan et al. 2003a, b). In a follow-up experiment this type of grooves have been Ni electroplated to form high aspect ratio Ni molds for nano-imprinting. These Ni mold features 100 nm wide and 2 μm tall walls (Ansari et al. 2004). Direct proton beam written sub-100 nm details have only been obtained in negative resists like SU-8 and HSQ (van Kan et al. 2004, 2006), featuring 60 nm and 22 nm wide lines respectively.

The newly developed second generation PBW beam line has the capability of high demagnification, which results in obtaining proton beam with a spatial resolution of $19.0 \times 29.9 \text{ nm}^2$ and single line scans with beam width

Y. Yao · P. Santhana Raman · J. A. van Kan (✉)
Department of Physics, CIBA, NUS, Singapore 117542,
Singapore
e-mail: phyjavk@nus.edu.sg

of 12.6 nm (van Kan et al. 2012). In this paper we present the first lithographic results with this new beam line which includes grooves written in PMMA down to 65 nm in width and 19 nm wide lines in HSQ. An outlook highlighting some of the improvements needed to further minimize the beam spot sizes is given.

2 Experiment

2.1 Hardware

The proton beam is provided by a 3.5 MV High Voltage Engineering Europa Singletron™ ion accelerator. The accelerator has a 10 eV energy stability (Mous et al. 1997) guaranteeing low chromatic aberrations. The beam optical system follows the normal layout of microprobe formation that of a demagnifying image of the beam passing through an object aperture. In our case we use two sets of differential micrometer controlled beam apertures, one serving as object aperture (Oxford Microbeams Ltd. OM10) and the other as downstream collimator slit (home built system), to control beam aberrations. The beam is scanned using a home built electrostatic scanning system and is focused using a magnetic lens system made up of three compact OM52 quadrupole lenses. To allow for high demagnification, the system is operated in a spaced Oxford triplet configuration (Grime and Watt 1984) with an object distance of 7.5 m and an image distance of 30 mm. This results in a system demagnification of 857×130 in X and Y, respectively. In this configuration the beam has a maximum scan area of $120 \times 120 \mu\text{m}^2$. Samples are mounted on a XYZ PI nano-positioning stage (N-310K059). The stage has a travel range of 20 mm in all directions and a 4 nm closed loop resolution in X and Y direction. To guarantee accurate sample placement in the focal plane, we have installed a 1 μm resolution closed loop laser displacement sensor along the Z axis (Omron, ZS-HLDC11). Ray trace calculation (PBO-LAB 3.0) shows that the spot size of a 2 MeV proton beam, passing through object and collimator slits (10×6 and $30 \times 30 \mu\text{m}^2$ opening respectively), will broaden 3 nm in X direction and less than 1 nm in Y direction at a distance of 1 μm from the focal plane.

A 2 μm thick Ni grid produced using proton beam writing (Watt et al. 2002; van Kan et al. 2005), is used to determine the beam spot size through scanning transmission ion microscopy (STIM) (Levi-Setti et al. 1974). To obtain orthogonal beam scanning, the magnetic quadrupole lens system and the scanning system are accurately aligned with respect to the X and Y axis of the PI sample stage using STIM analysis of the Ni grid.

Stage scanning software has been developed using National Instruments LABVIEW. Beam scanning and beam blanking using ion scan software are controlled through a

National Instruments PXI 6259 card (Bettiol et al. 2005). In the stage scanning method the software allows the users to move the stage in X or Y direction, while scanning the focused proton beam perpendicular to the stage movement. In the case of stitching, the beam is scanned over the first field, next the stage moves to a new position and the beam scans the second field. Now in the second generation PBW system, stitching and a combination of beam plus stage scanning facilitates large area fabrication of micro or nano structures, like long waveguides, microfluidic channels and resolution standards (Watt et al. 2007; Yao et al. 2013).

2.2 Lithography

In the PBW experiments presented here, PMMA positive resist (MW 950 kD, A11 Mircochem) and HSQ negative resist (XR-1541, Dow corning) were used. The 2 μm PMMA layers were spin coated on silicon substrate, which was pre-coated with 30 nm Cr and 30 nm Au (as seed layer for Ni electroplating) by magnetron sputter deposition. During PBW a dose of 100–200 nC/mm² was used for PMMA exposure using 1 or 2 MeV protons. After exposure, the samples were developed in an IPA:DI water mixture (7:3 by volume) for 2.5 min followed by a DI water rinse. In order to overcome the inherent charging issues while imaging PMMA polymer films using a scanning electron microscope (SEM), some of the fine features in PMMA were Ni electroplated (using Ni-sulfamate solution) followed by PMMA removal in acetone before SEM analysis. Due to the good adhesion between HSQ and silicon substrate, 100 nm thick HSQ layer was directly spin coated on a silicon substrate for 30 s at 3,000 rpm. The sample was prebaked for 120 s at 150 °C before the proton beam exposure. After exposure the sample was developed in a 2.38 % tetramethylammonium hydroxide (TMAH) solution for 60 s followed by a DI water rinse.

3 Results and discussion

To test the quality of the combined stage plus beam scanning mode, a grid pattern was written in the PMMA layer. To write the vertical lines a focused beam of 2 MeV protons ($200 \times 500 \text{ nm}^2$) is scanned across 2 μm in the X direction while the PI stage moves 200 μm along the vertical direction at 1 $\mu\text{m/s}$. To generate the horizontal lines the same beam is scanned in Y and the stage is moved along the horizontal direction. After development and Ni electroplating, an orthogonal Ni grid ($90.0^\circ \pm 0.1^\circ$) is obtained, as shown in Fig. 1a.

To evaluate the stitching and the orthogonality of beam scanning, 10 μm long cross lines were written in four fields (shown in Fig. 1b). The cross lines were written in the HSQ

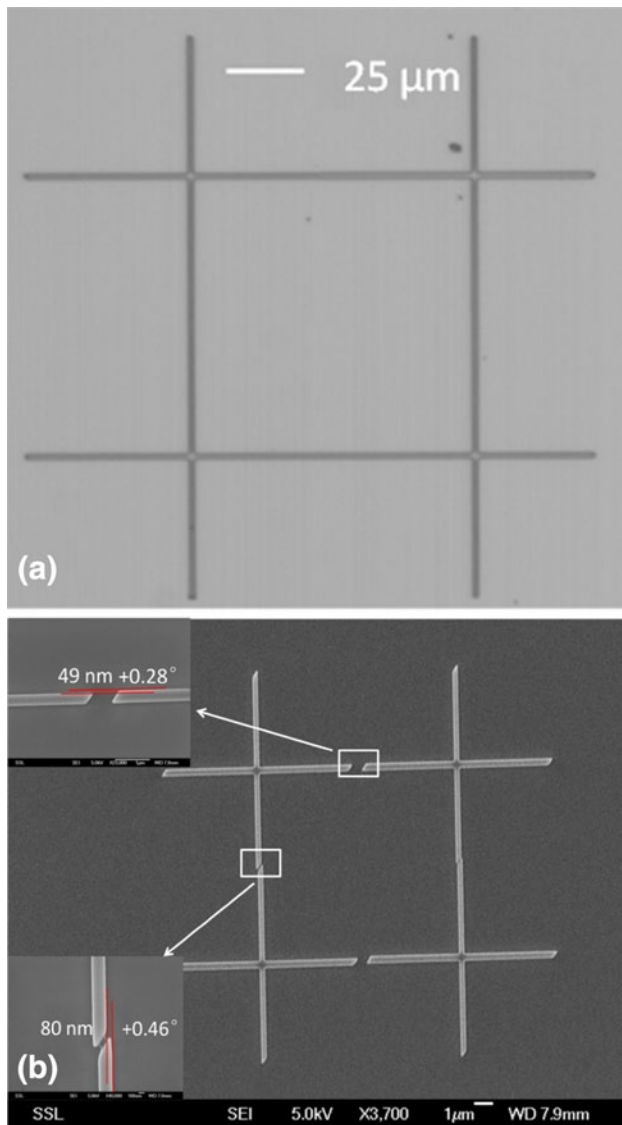


Fig. 1 **a** Optical image of 2 μm wide, 200 μm long orthogonal Ni lines produced by stage scanning during PBW and later electroplated. **b** Four HSQ cross lines, 10 μm long produced by stitching method, with insets showing the error in stitching

layer with a focused 2 MeV proton beam ($200 \times 300 \text{ nm}^2$). The four fields were exposed sequentially by moving the stage in X or Y direction appropriately. We can notice, from the insets, that there is a stitching error of about 80 nm (which corresponds to an offset by $+0.46^\circ$) in X direction and 49 nm (corresponding to $+0.28^\circ$ offset) in Y direction between the end of the lines in neighbouring fields, thus featuring an overall orthogonality of $90.00^\circ \pm 0.18^\circ$. The error is due to the combined effect of scan size calibration, alignment accuracy of the scanning system as well as lens movement due to thermal fluctuation.

A focused 1 MeV H_2^+ beam (with a beam spot size of $50 \times 70 \text{ nm}^2$) was used to write parallel lines by exposing

PMMA to different doses. Each set of lines are digitized using $4,096 \times 4,096$ pixels in a writing field of $60 \times 60 \mu\text{m}^2$ (using ION SCAN software), where each line is a single pixel wide in X direction. After development and electroplating the Ni lines are imaged in the SEM (see Fig. 2).

At an exposure dose of 6.7×10^3 protons/ μm along a line the resist was found to be not completely soluble during the development process. Whereas when the dose was increased to 1.3×10^4 protons/ μm , a groove with a width of about 65 nm in PMMA was written and after electroplating a 65 nm wide Ni line was obtained (Fig. 2a). The size of this feature closely matches the proton beam width in X direction. It is worthwhile mentioning that this (65 nm) is the smallest lithographic groove fabricated on PMMA by PBW, until-to-date. The waviness observed at the edges of this PBW structure could be primarily related to the instability of proton beam current due to the accelerator-tuning. Further when the dose was increased to 2.0×10^4 , 2.7×10^4 and 3.3×10^4 protons/ μm , the resultant structures on PMMA are 75, 84 and 106 nm respectively (Fig. 2b–d respectively). The Ni line width is found to increase with proton exposure dose. This broadening is due to contribution of the tailing portion of Gaussian shaped proton beam profile, which reaches sufficient exposure dose for bond-scissioning in PMMA. These results imply that the structure size obtained by PBW depends on the beam size and optimal dose, along with other factors (Bolhuis et al. 2009; Grigorescu and Hagen 2009).

In a next experiment, parallel line pattern were written on HSQ layer with a focused 2 MeV proton beam (see Fig. 3). The pattern was digitized using $2,048 \times 2,048$ pixels in a writing field of $32 \times 32 \mu\text{m}^2$, where each line was one pixel wide and the spacing was 4 pixels wide. The beam was focused down to 20 nm in X direction and exposed onto the HSQ to a dose of $30 \text{ nC}/\text{mm}^2$ (3.75×10^3 protons/ μm). After development, a line width of 19 nm (noted to be the smallest structure written by PBW) and a spacing of 60 nm was obtained, closely matching the experimental parameters (as indicated in Fig. 3).

4 Summary and outlook

The second generation proton beam writing facility developed at CIBA has been improved and can now produce high quality lithographic structures on different resist materials. A few developmental activities associated with this PBW beam line were discussed, e.g. alignment of electrostatic scan plates and quadrupole lenses and incorporation of a closed loop in Z direction for the sample-stage movement. The possibility of large area PBW has been demonstrated through stitching as well as combined stage and beam scanning mode. Orthogonal (90.0°) and fine

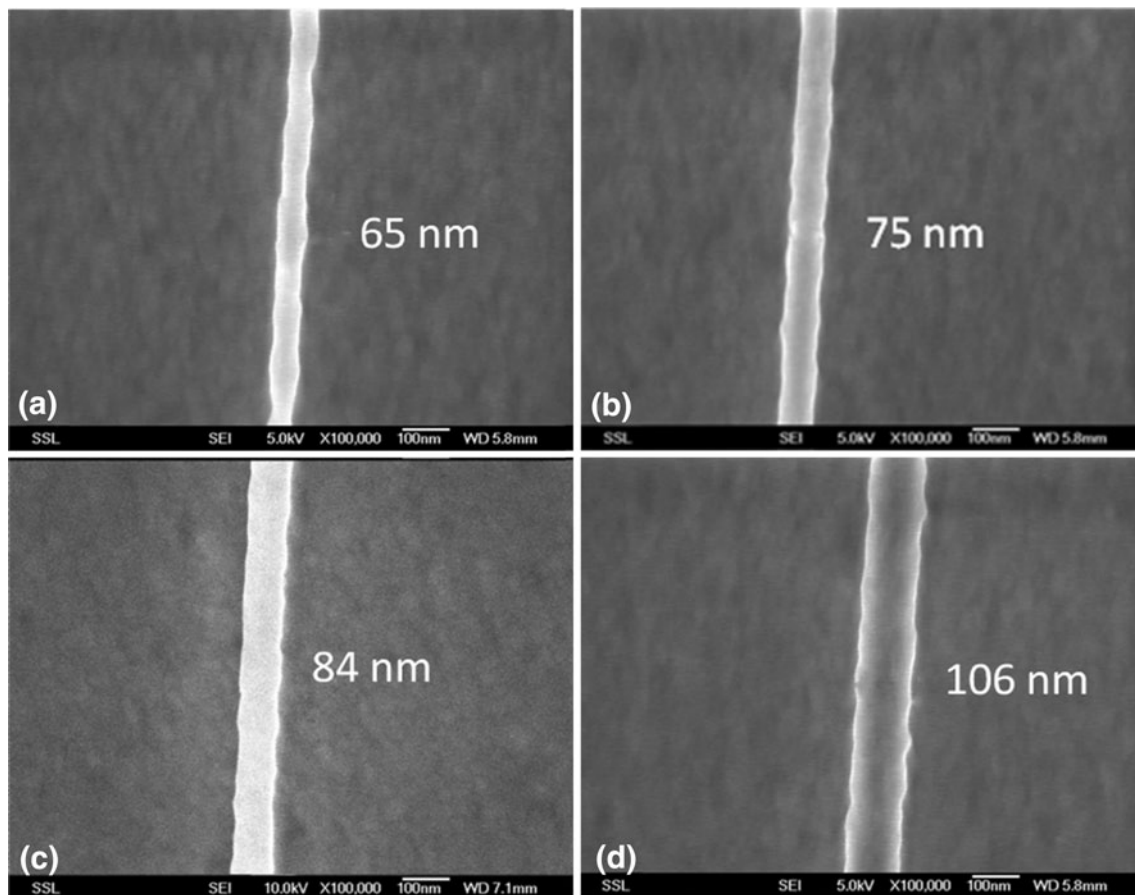


Fig. 2 SEM images of Ni lines fabricated via electroplating on a 2 μm thick PMMA sample subjected to 1 MeV H_2^+ beam exposure to different doses along the lines for **a** 1.3×10^4 protons/ μm , **b** 2.0×10^4 protons/ μm , **c** 2.7×10^4 protons/ μm and **d** 3.3×10^4 protons/ μm

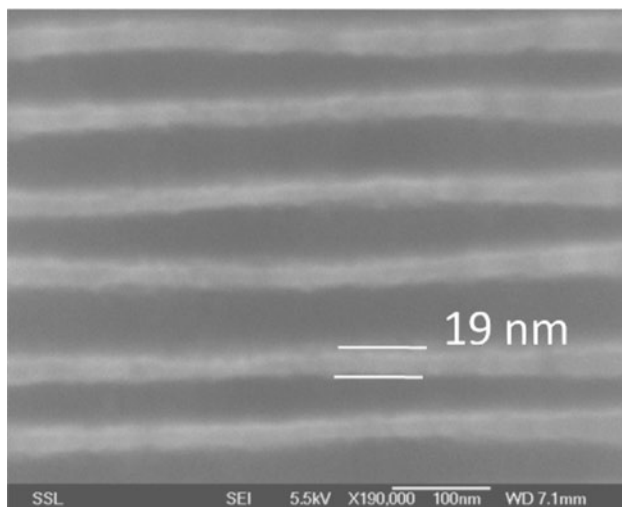


Fig. 3 SEM images of 19 nm line width with a spacing of 80 nm on 100 nm thick HSQ sample written by 2 MeV proton beam

lithographic structures on PMMA down to 65 nm and on HSQ down to 19 nm are demonstrated, these HSQ lines are the smallest features ever written in PBW.

One major limitation in achieving better resolution is the lack of a high brightness ion source, which is currently under development in collaboration with Delft University (Jun and Kruit 2011). Thermal fluctuation in the lens system results in beam drift along the Y direction, which hampers proton beam focusing in Y direction. To reduce this drift, a vortex fan is used to stabilize the lens temperature within ± 0.1 $^{\circ}\text{C}$, allowing the fabrication of 19 nm wide lines. We are also working on better ways to reduce thermal fluctuation. Moreover to attain small proton beam written structures we aim to optimise other factors such as an appropriate photoresists, optimal dose and developer.

Acknowledgments The authors acknowledge the financial support rendered by the US air force, Japan office and MOE, Singapore (R-144-000-265-112).

References

- Ansari K, van Kan JA, Bettiol AA, Watt F (2004) Fabrication of high aspect ratio 100 nm metallic stamps for nanoimprint lithography using proton beam writing. *Appl Phys Lett* 85:476–478
- Bettiol AA, Udalagama CNB, van Kan JA, Watt F (2005) Ionscan: scanning and control software for proton beam writing. *Nucl Instrum Meth Phys Res B* 231:400–406
- Bolhuis S, van Kan JA, Watt F (2009) Enhancement of proton beam writing in PMMA through optimization of the development procedure. *Nucl Instrum Meth Phys Res B* 267:2302–2305
- Grigorescu AE, Hagen CW (2009) Resists for sub-20-nm electron beam lithography with a focus on HSQ: state of the art. *Nanotechnology* 20:292001
- Grime GW, Watt F (1984) Beam optics of quadrupole probe forming systems. Adam Hilger, Bristol
- Jun D, Kruit P (2011) Ion beams in SEM: an experiment towards a high brightness low energy spread electron impact gas ion source. *J Vac Sci Technol B* 29:06F603-1–06F603-7
- Levi-Setti R (1974) Proton scanning microscopy: feasibility and promise. *Scanning Electron Microsc* 125–134
- Mous JW, Haitisma RG, Butz T, Flammeyer RH, Lehmann D, Vogt J (1997) The novel ultrastable HVEE 3.5 MV Singletron™ accelerator for nanoprobe applications. *Nucl Instrum Meth Phys Res B* 130:31–36
- Rothschild M, Goodman RB, Hartney MA, Horn MW, Kunz RR, Sedlacek JHC, Shaver DC (1992) Photolithography at 193 nm. *J Vac Sci Technol B* 10:2989–2996
- Teo EJ, Breese MBH, Tavernier EP, Bettiol AA, Watt F, Liu MH, Blackwood DJ (2004) Three-dimensional microfabrication in bulk silicon using high-energy protons. *Appl Phys Lett* 84:3202–3204
- Udalagama CNB, Bettiol AA, Watt F (2009) Stochastic spatial energy deposition profiles for MeV protons and keV electrons. *Phys Rev B* 80:224107-1–224107-8
- van Kan JA, Bettiol AA, Watt F (2003a) Proton beam nano-machining: end station design and testing. *Mater Res Soc Symp Proc* 777:T2.1.1–T2.1.10
- van Kan JA, Bettiol AA, Watt F (2003b) Three dimensional nanolithography using proton beam writing. *Appl Phys Lett* 83:1629–1631
- van Kan JA, Bettiol AA, Ansari K, Teo EJ, Sum TC, Watt F (2004) Proton beam writing: a progress review. *J Int Nanotechnol* 1:464–479
- van Kan JA, Shao PG, Molter P, Saumer M, Bettiol AA, Osipowicz T, Watt F (2005) Fabrication of a free standing resolution standard for focusing MeV ion beams to sub 30 nm dimensions. *Nucl Instrum Meth Phys Res B* 231:170–175
- van Kan JA, Bettiol AA, Watt F (2006) Proton beam writing of 3D nanostructures in hydrogen silsesquioxane. *Nano Lett* 6:579–582
- van Kan JA, Shao PG, Ansari K, Bettiol AA, Osipowicz T, Watt F (2007) A tool for high-aspect ratio mask production. *Microsyst Technol* 13:431–434
- van Kan JA, Malar P, Baysic de Vera A, Chen X, Bettiol AA, Watt F (2011) Proton beam writing nanoprobe facility design and first test results. *Nucl Instrum Meth Phys Res A* 645:113–115
- van Kan JA, Malar P, Baysic de Vera A (2012) The second generation Singapore high resolution proton beam writing facility. *Rev Sci Instrum* 83:02B902-1–02B902-3
- Watt F, Rajta I, van Kan JA, Bettiol AA, Osipowicz T (2002) The second generation Singapore high resolution proton. *Nucl Instrum Meth Phys Res B* 190:306–311
- Watt F, van Kan JA, Rajta I, Bettiol AA, Choo TF, Breese BH, Osipowicz T (2003) The National University of Singapore high energy ion nano-probe facility: performance tests. *Nucl Instrum Meth Phys Res B* 210:14–20
- Watt F, Breese BH, Bettiol AA, van Kan JA (2007) Proton beam writing. *Mater Today* 10:20–29
- Yao Y, Mourik MWV, Santhana Raman P, van Kan JA (2013) Improved beam spot measurements in the 2nd generation proton beam writing system. *Nucl Instrum Meth Phys Res B* 306:265–270