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Proton beam micromachined buried microchannels in negative tone resist materials

I. Rajta [a,*], M. Chatzichristidi [b], E. Baradács [c], C. Cserháti [d], I. Raptis [b], K. Manoli [b], E.S. Valamontes [e,f]

[a] Institute of Nuclear Research of the Hungarian Academy of Sciences, P.O. Box 51, H-4001 Debrecen, Hungary
[b] Institute of Microelectronics, NCSR-"Demokritos", 153 10 Aghia Paraskevi, Greece
[c] Department of Environmental Physics, University of Debrecen, Poroszlay u. 6, H-4026 Debrecen, Hungary
[d] Department of Solid State Physics, University of Debrecen, P.O. Box 2, H-4010 Debrecen, Hungary
[e] Department of Telecommunications, University of Peloponnese, GR-22100 Tripoli, Greece
[f] Department of Electronics, Technological and Educational Institute of Athens, 12210 Aegaleo, Greece

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Abstract

In the present work the Atomki, Debrecen microprobe facility has been used to write long tilted structures by 2 MeV protons. For the formation of the structures, two exposures have been carried out at +20° and −20° using a goniometer stage sample holder. The tilted structures were resolved in the negative tone resist materials SU-8 and ADEPR (an aqueous base developable chemically amplified resist). The length of the microchannels was varied between 100 μm and 1000 μm, the wall thickness was less than 10 μm. By applying the developed methodology it was possible to resolve the desired layout through the whole length of the channel.
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1. Introduction

Tilted structures in either thin or thick films are very interesting for various applications such as photonic crystals and microchannels [1–3]. In addition, such structures could be also used for gas/liquid handling on chips (e.g. [4]).

Fabrication of thick tilted structures is a challenging task for conventional lithographic technologies. In the case of optical lithography, if the sample is placed with a wedge to the mask then the resolution of the final structures will be seriously deteriorated due to the gap between the mask and the resist film [5]. In addition, tilted exposures require specially designed stages not available in common mask aligners. Another way to fabricate tilted structures is with the use of grey scale masks [6], where the mask's transmittance defines the final resist thickness remaining on the substrate after the development. However, in this approach the fabrication of open microchannels is not obvious. In addition, interference lithography has been proved capable to resolve tilted structures of very fine resolution [7] over a large area with negligible defects at a limited exposure time. However, the required set-up is quite expensive and has limited capabilities on angle and distance between adjacent structures.

In the case of electron beam lithography the penetration depth of electrons is limited and the electron beam broadens significantly as the electrons travel in large depths. Thus electron beam irradiation is inappropriate for the fabrication of tilted structures especially in thick films. In addition, tilted exposures require stages with tilt capabilities available only in SEM converted electron beam lithography (EBL) tools and not in standard EBL tools.

* Corresponding author. Tel.: +36 52 509200; fax: +36 52 416181.
E-mail address: rajta@atomki.hu (I. Rajta).

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X-ray lithography has been proved capable to produce tilted structures of very fine resolution [8]. However, in that technology a delicate mask is required, which is very expensive. The cost of the X-ray source (synchrotron) is also very high. Therefore the application of X-ray lithography for the fabrication of tilted structures is inappropriate for research when the layout is not final.

The use of proton beam irradiation has already been proved successful to the patterning of thick resist films with very high aspect ratio and vertical sidewalls of the resist features [9]. Proton beam writing (PBW) is promising for the fabrication of tilted structures due to the fact that the proton beam does not broaden too much due to the interaction with matter for a large depth. An example of this fact is that a 2 MeV proton beam allows the patterning of 50 μm thick resist films without significant increase of beam diameter even at the bottom of such a thick layer. In addition, this is a maskless process (the proton beam scans over selected areas in a direct write manner), which is an advantage for research applications. In order to produce embedded microchannels in negative resist, double exposure using different energies has been proven a successful method [10–13], however in this case there are several complications (i.e. the need to wait for the beam energy to stabilize twice, need to focus and calibrate twice, etc.). Alternatively, a closed nanochannel has been formed by PBW on PMMA film subsequently covered with two PMMA sheets by thermal bonding [14].

In the present work, high resolution and high aspect ratio polymeric structures patterned on the nuclear microprobe facility at ATOMKI, Debrecen, Hungary are resolved in standard SU-8 [15] and ADEPR (aqueous developed negative resist) [16,17] are presented. The developed technology is further applied for the fabrication of buried microchannels with tilted sidewalls clear from one end to the other with critical dimensions less than 10 μm by exploiting a goniometer set-up.

2. Experimental

All irradiations in this work have been performed on the nuclear microprobe facility at ATOMKI, Debrecen, Hungary [18]. The proton energy used for all exposures was 2 MeV. Beam currents of 5–60 pA were focussed down to 2–3 μm spotsize. The scan size was typically 1000 μm and the beam step size was 1 μm. The delivered fluence was measured using the backscattering signals from the samples by a PIN diode array [19], allowing pixel normalization. The beam scanning was done using a National Instruments (NI) card (model 6711), and the *Ion-Scan* software package developed specifically for PBM applications [20].

A goniometer stage (Thermo Vacuum Generators 5-axis HPT slide goniometer) was fitted in the sample holder and exposures with an angle from beyond −180° to +180° between the beam and the sample normal could be carried out. The angle resolution and accuracy is 0.01°.

In the present work, proton beam writing on two negative chemically amplified resists is explored. The first resist is an epoxy based resist with the commercial name of SU-8 (purchased from MicroResist GmbH) [21]. The second resist is an aqueous base developable (IC standard aqueous developers (tetramethyl ammonium hydroxide – TMAH 0.26N)) epoxy resist based on a specific grade epoxy novolac (EP) polymer, a partially hydrogenated poly-4-hydroxy styrene (PHS) polymer, and an onium salt as photoacid generator (PAG). The latter resist has primarily been developed for UV-LIGA [16] and its formulation has been recently optimized by our group for proton beam lithography [17]. The formulation for P-beam writing consists of 35% (w/w) total polymer concentration in ethyl(s)-lactate. The polymer was a mix of 78% (w/w) PHS with 12% degree of hydrogenation and 22% (w/w) EP. The used PAG was 1-(4-hydroxy-3-methylphenyl) tetrahydrothiophenium triflate (o-CS-triflate) 3% (w/w) with respect to the total polymer concentration. The processing conditions of both resists are given in Tables 1 and 2, respectively.

The thermal transition properties (T_g) of the PHS (hydrogenation 12%)-EP mixture (78–22% w/w in ethyl lactate) film and of the unexposed and exposed ADEPR system film were measured using a modulated differential scanning calorimetry (MDSC 2920, TA Instruments). The PHS–EP mixture exhibits one T_g at 108 °C showing that the two components of the system are practically fully mixed. The unexposed ADEPR system also exhibits one T_g

Table 1
Sample preparation and processing conditions for SU-8 photoresist

Step	Conditions for SU-8
Coating	Spinning at 500 rpm/7 s plus 3000 rpm/30 s
Post apply bake	65 °C/5 min plus 95 °C/15 min and subsequent cooling down on a levelled hotplate (film thickness 40 μm)
Exposure	2 MeV Protons, beam currents 5–60 pA, 2–3 μm spot size, 1000 μm scan size Fluence measurements: backscattering signals, by PIN detector array, total area 400 mm^2 High count rate → pixel normalisation
Post exposure bake	65 °C/1 min plus 95 °C/4 min and subsequent cooling down on a levelled hotplate
Development	PGMEA (22 °C)
Rinsing	IPA for 30 s

Table 2
Sample preparation and processing conditions for ADEPR photoresist

Step	Conditions for ADEPR
Coating	Spinning at 600 rpm/20 s (solution 35%)
Post apply bake	95 °C/45 min and subsequent cooling down (film thickness 35 μm)
Exposure	Same parameters as above
Post exposure bake	110 °C/8 min and subsequent cooling down
Development	AZ726 MIF (22 °C)
Rinsing	DI water for 30 s
Stripping	Acetone in ultrasonic bath

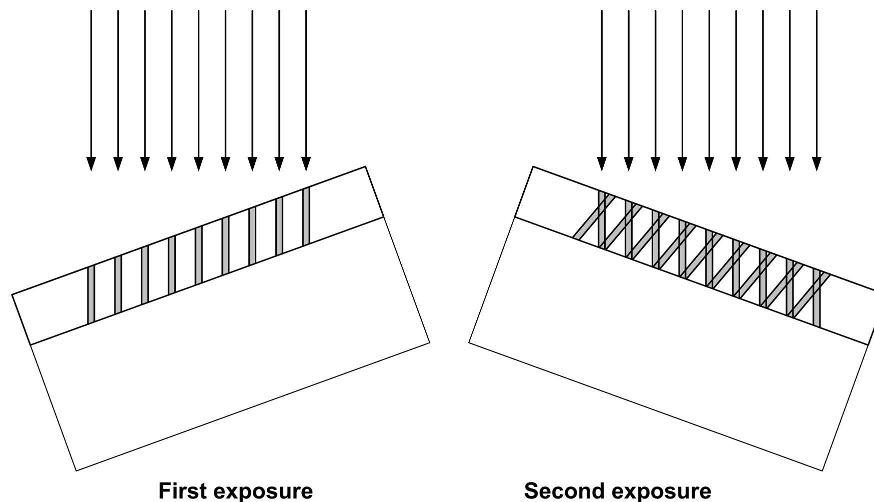

Fig. 1. Schematic representation of the titled exposures using the goniometer set-up (Thermo Vacuum Generators 5-axis HPT slide goniometer). The sample was tilted to +20° for the first irradiation, then −20° for the second irradiation, and kept a well-defined alignment point in the microscope view to make sure that the two irradiations will overlap.

at 88 °C whereas the exposed film did not exhibit any T_g until 300 °C. The T_g of the unexposed ADEPR system is lower than the one of the PHS-EP mixture possibly because the PAG, that is a small molecule, acts as a plasticizer. Again the exhibition of one only T_g proves that the system is practically fully mixed. The fact that the exposed ADEPR film exhibits no T_g can be attributed to the cross-linking of the system.

For the fabrication of long straight microchannels in negative resist we propose a method that is easier than irradiation with two different energies. First, the Si wafer with the resist was irradiated under +20° tilt to the normal of the sample. When the exposure was completed, a second irradiation followed under −20° tilt. In order to make sure that the structures will overlap a well-defined alignment point was kept on the microscope view. This alignment process ensures that the sample was not moved along the beam axis, which is important in order to keep the beam focus on the sample surface, and finally it was possible to have alignment accuracy of few micrometers. The samples were finally removed from the chamber, post exposure baked and developed. In this way a lambda structure shaped microchannel was fabricated. The schematic view of the exposure strategy is shown in Fig. 1.

The evaluation of the final structures was performed in the Institute of Microelectronics, NCSR 'Demokritos' on a *LEO 440* SEM and in the Department of Solid State Physics (UniDeb-Atomki Atomic Force and Electronmicroscope Laboratory) in Debrecen on a *Hitachi S-4300CFE* SEM.

3. Results and discussion

3.1. Single pixel and single line exposures

First, single pixel pillars and single pixel lines of both negative resists were fabricated in order to optimize the processing conditions and examine the aspect ratio of the resulted pillars. These test exposure layouts were the basis of the tilted structures and they were performed to make sure that we can produce high resolution and high aspect ratio walls of single line irradiations.

In Figs. 2 and 3 typical SEM images of these exposures are shown for SU-8 and ADEPR respectively. Both resists resulted single pillars with a smallest diameter of 2.7 μm in SU-8, and 2.8 μm in ADEPR. The achieved smallest

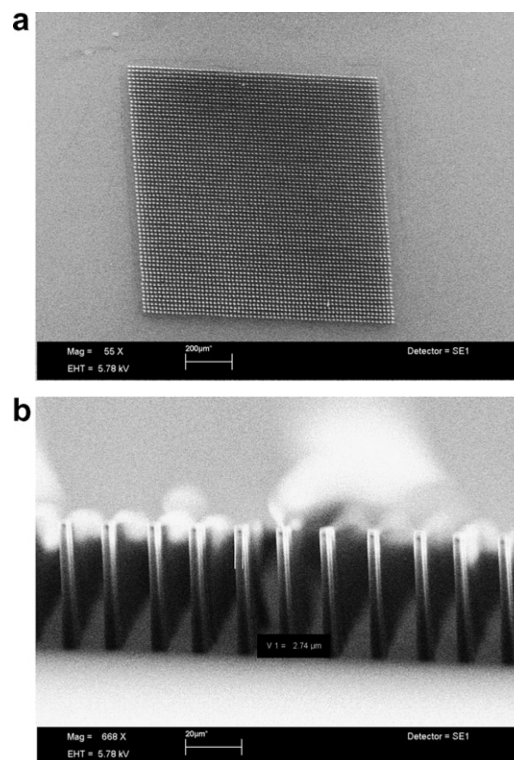

Fig. 2. Pillars fabricated with single pixel irradiation of SU-8. (a) Top view of 1 mm^2 area of single pixel irradiation and (b) side view of Fig. 2(a). The resolution of the pillars is 2.7 μm and the aspect ratio is 14.

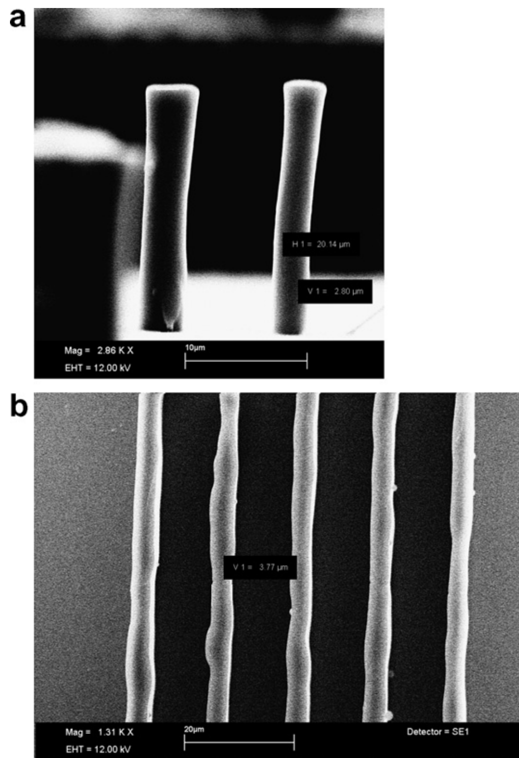

Fig. 3. (a) Side view of pillars of single pixel irradiation of ADEPR. The resolution of the pillars is 2.8 μm and the aspect ratio is 7. (b) Top view of single line irradiation on ADEPR. The width of the lines is 3.8 μm.

feature size was the same as the measured beam spot size. In Fig. 2, it is noticeable that the matrix of the SU-8 pillars is highly ordered without defects. The highest aspect ratio achieved for this type of structures was 14 for SU-8, and 7 for ADEPR. In Fig. 3 a series of ADEPR lines with vertical walls are shown. All the structures mentioned above are fully developed.

3.2. Lambda structures

In Fig. 4, side view of developed microchannels is shown. Two exposures were performed in each sample using the goniometer of the microbeam chamber. Given that the proton energy was 2 MeV, the resist thickness was chosen so as to enable the protons to reach the silicon substrate (the effective thickness of the resist was more than the nominal thickness due to the sample tilt). The length of the microchannels showed in Fig. 4 is 100 μm, the wall thickness is about 7.5 μm and the resist thickness is 40 μm. It can be seen that the microchannels are fully developed and exhibits tilted sidewalls, each with uniform thickness from top to bottom. Fig. 5 shows the sample (when viewed along the beam direction) during the second irradiation, i.e. the angle between the sample normal and the beam was −20°, while the first irradiation was performed at +20°. The sample was developed at once after both irradiations finished.

As it has been proved recently [22], it is possible to fabricate 1.6 mm long microchannels by removing unexposed

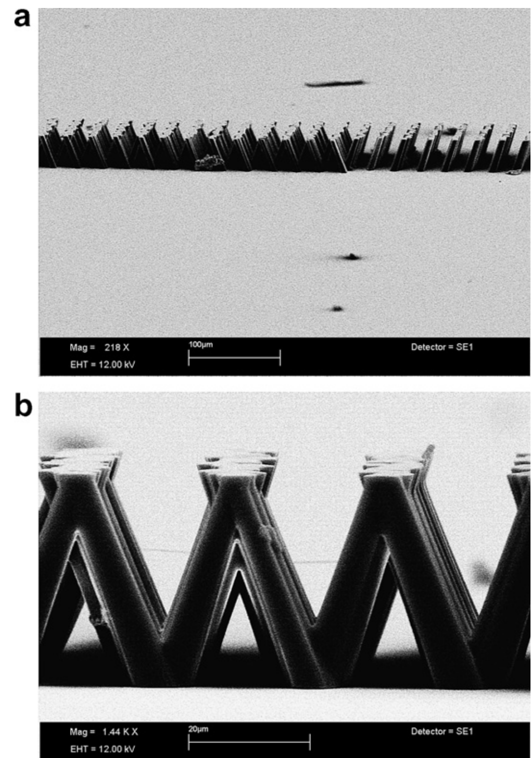

Fig. 4. Side view of the 'lambda' structures of SU-8. The length of the channel is 100 μm and the wall thickness is 10 μm. (a) At low magnification and (b) at high magnification. (It is visible that the buried channels are open, i.e. they can be applied to transport fluids or gases.)

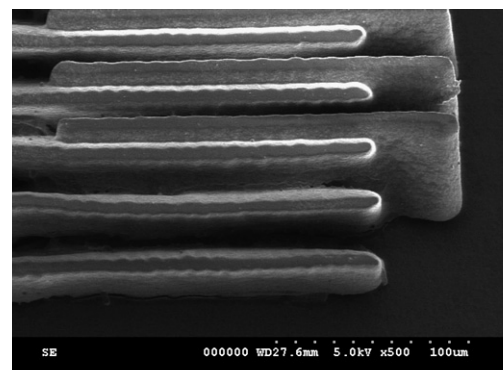

Fig. 5. −20° View of the 'lambda' structure. This image shows the sample (when viewed along the beam direction) during the second irradiation, i.e. the angle between the sample normal and the beam was −20°, while the first irradiation was performed at +20°. The sample was developed at once after both irradiations finished. (It is also visible here that the tilted sidewalls forming the buried channels are continuous.)

resist during the development. Therefore it is possible to resolve at least such long channels with the proposed methodology.

4. Conclusions

Proton beam writing was performed at the Institute of Nuclear Research of the Hungarian Academy of Sciences (Atomki) on negative tone resist materials, such as the con-

ventional SU-8 and ADEPR an aqueous base developable chemically amplified resist.

Single pixel pillars, single lines of walls were irradiated at normal incidence. The achieved smallest feature size was the same as the measured beam spot size, the highest aspect ratio was 14 for the samples of SU-8 and 7 for the samples of ADEPR.

Wall type (single line) irradiations have been irradiated at $\pm 20^\circ$ tilted sample such that the irradiations overlapped. This way 'lambda' structures were produced, i.e. another way of producing covered microchannels at various lengths was demonstrated. For a system of straight long microchannels, the proposed methodology offers an alternative compared to the complicated method of the two-energy exposure.

The proposed methodology could be applied for the implementation of 'fence' structures and could be further extended to the fabrication of particular photonic structures, such as Yablonovite-type [23,24], by an additional exposure (three in total) to a third axis. In that particular application the main issue will be the alignment between the three exposures.

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References

[1] A.A. Bettiol, T.C. Sum, J.A. van Kan, F. Watt, Nucl. Instr. and Meth. B 210 (2003) 250.
[2] A.A. Bettiol, T.C. Sum, F.C. Cheong, C.H. Sow, S. Venugopal Rao, J.A. van Kan, E.J. Teo, K. Ansari, F. Watt, Nucl. Instr. and Meth. B 231 (2005) 364.
[3] K.A. Mahabadi, I. Rodriguez, S.C. Haur, J.A. van Kan, A.A. Bettiol, F. Watt, J. Micromech. Microeng. 16 (2006) 1170.
[4] F. Romanato, M. Tormen, L. Businaro, L. Vaccari, T. Stomeo, A. Passaseo, E. Di Fabrizio, Microelectron. Eng. 73–74 (2004) 870.
[5] W.M. Moreau, Semiconductor Lithography. Principles, Practices, and Materials, Plenum Press, New York, 1988.
[6] A.C. Cefalas, P. Argitis, Z. Kollia, E. Sarantopoulou, T.W. Ford, A.D. Stead, A. Marranca, C.N. Danson, J. Knott, D. Neely, Appl. Phys. Lett. 72 (1998) 3258.
[7] J.H. Moon, J. Ford, S. Yang, Polym. Advan. Technol. 17 (2006) 83.
[8] G. Feiertag, W. Ehrfeld, H. Freimuth, H. Kolle, H. Lehr, M. Schmidt, M.M. Sigalas, C.M. Soukoulis, G. Kiriakidis, T. Pedersen, J. Kuhl, W. Koenig, Appl. Phys. Lett. 71 (1997) 1441.
[9] F. Watt, A.A. Bettiol, J.A. van Kan, E.J. Teo, M.B.H. Breese, Int. J. Nanosci. 4 (2005) 269.
[10] F.E.H. Tay, J.A. van Kan, F. Watt, W.O. Choong, J. Micromech. Microeng. 11 (2001) 27.
[11] J.A. van Kan, J.L. Sanchez, T. Osipowicz, F. Watt, Microsyst. Technol. 6 (2000) 82.
[12] T. Osipowicz, J.A. van Kan, T.C. Sum, J.L. Sanchez, F. Watt, Nucl. Instr. and Meth. B 161–163 (2000) 83.
[13] J.A. van Kan, A.A. Bettiol, K. Ansari, F. Watt, Proc. SPIE 4343 (2001) 466.
[14] P.G. Shao, J.A. van Kan, L.P. Wang, K. Ansari, A.A. Bettiol, F. Watt, Appl. Phys. Lett. 88 (2006) 093515.
[15] J.A. van Kan, J.L. Sanchez, B. Xu, T. Osipowicz, F. Watt, Nucl. Instr. and Meth. B 158 (1999) 179.
[16] M. Chatzichristidi, I. Raptis, P. Argitis, J. Everett, J. Vac. Sci. Technol. B 20 (2002) 2968.
[17] I. Rajta, E. Baradács, M. Chatzichristidi, E.S. Valamontes, I. Uzonyi, I. Raptis, Nucl. Instr. and Meth. B 231 (2005) 423.
[18] I. Rajta, I. Borbély-Kiss, Gy. Mórik, L. Bartha, E. Koltay, Á.Z. Kiss, Nucl. Instr. and Meth. B 109 (1996) 148.
[19] G.Á. Szíki, E. Dobos, Zs. Kertész, Z. Szikszai, I. Uzonyi, Á.Z. Kiss, Nucl. Instr. and Meth. B 219 (2004) 420.
[20] A.A. Bettiol, C.N.B. Udalagama, J.A. van Kan, F. Watt, Nucl. Instr. and Meth. B 231 (2005) 400.
[21] http://www.microchem.com/products/pdf/SU8_50-100.pdf.
[22] M. Kitsara, M. Chatzichristidi, D. Niakoula, D. Goustouridis, K. Beltsios, P. Argitis, I. Raptis, Microelectron. Eng. 83 (2006) 1298.
[23] G.J. Schneider, E.D. Wetzel, J.A. Murakowski, D.W. Prather, Proc. SPIE 5720 (2005) 9.
[24] C. Cuisin, A. Chelnokov, J.-M. Lourtioz, D. Decanini, Y. Chen, Appl. Phys. Lett. 77 (2000) 770.