ELSEVIER
Nuclear Instruments and Methods in Physics Research B 158 (1999) 179–184
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.nl/locate/nimb

Resist materials for proton micromachining

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Abstract

The production of high aspect ratio microstructures is a potential growth area. The combination of deep X-ray lithography with electroforming and micromolding (i.e. LIGA) is one of the main techniques used to produce 3D microstructures. The new technique of proton micromachining employs focused MeV protons in a direct write process which is complementary to LIGA, e.g. micromachining with 2 MeV protons results in microstructures with a height of 63 μm and lateral sub-micrometer resolution in PMMA resist. The aim of this paper is to investigate the capabilities of proton micromachining as a lithographic technique. This involves the study of different types of resists. The dose distribution of high molecular weight PMMA is compared with three other types of resist: First the positive photo resist AZ P4620 will be discussed and then PMGI SF 23, which can be used as a deep UV, e-beam or X-ray resist. Finally SU-8, a new deep UV negative type of chemically amplified resist will be discussed. All these polymers are applied using the spin coating technique at thicknesses of between 1 and 36 μm

PACS: 07.10.Cm; 07.78.+s; 85.40.Hp
Keywords: Micromachining; Nuclear microscope; High aspect ratio

1. Introduction

There is only a limited number of lithographic techniques able to produce high aspect ratio microstructures. The LIGA (LIthographie, Galvano, Abformung) process is one of the techniques currently being used to produce 3D microstructures [1,2]. High aspect ratio masks are irradiated in the LIGA process using synchrotron X-ray radiation. Because of the high costs involved (expensive synchrotron accelerator, complicated mask production process etc.) other 3D lithographic techniques are being developed, e.g. stereo micro lithography which allows the manufacture of 3D parts by a light-induced spatially resolved polymerization process [3], although a limitation of this technique is its rather low accuracy [4,5]. In order to develop 3D lithographies which do not require the high flux e.g. available only from a synchrotron, new types of resist are being developed. One of these is SU-8 [6], a chemically amplified negative tone resist which shows high potential because it can be used with UV radiation and proton micromachining [7] (see below). SU-8 has been

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used to produce microstructures with thicknesses up to a few mm.

In this paper proton micromachining will be shown to be a powerful tool in the production of detailed 3D microstructures. In the process MeV protons are used to irradiate different types of resists. Four different resist types will be compared; three positive and one negative resist. All resist layers are deposited on Si wafers and have thicknesses ranging from 1 up to 36 μm. An advantage of proton micromachining compared to other 3D lithographic techniques is that no mask is needed to produce structures with high aspect ratios and submicrometer detail in the lateral direction [8,9]. Examples of 3D microstructures produced with proton micromachining in positive resist and negative resist will be shown. Potential applications of proton micromachining are discussed in [10].

2. Experimental procedures

The lithographic work was carried out using the nuclear microscope at the Research Centre for Nuclear Microscopy at the National University of Singapore [11], where 100 nm spot sizes can be achieved for 2 MeV protons [12]. Typical currents used for micromachining range between 1 and 100 pA with a typical spot size of 1 μm^2. Details of the scanning system used for proton micromachining can be found elsewhere [7,9].

In order to reduce the effect of the beam intensity fluctuations caused by energy instabilities which are common in belt driven accelerators there are two options. One can normalize the proton dose for each pixel in the scan pattern using RBS [9] or use rapid repeated scanning. PMMA is rendered developable by an ion dose that corresponds in our set-up to 12 backscattering events per μm^2 with a dose latitude of approximately 20% [8]. Therefore this normalization procedure provides enough scission of molecular chains without excessively damaging the resist, resulting in smooth microstructures. Exposing the more sensitive resist SU-8 requires only about one backscatter event per μm^2. An approximately even dose distribution can then be obtained if many fast scans of a pattern are written (e.g. 100), thereby averaging the beam fluctuations over each pixel exposure resulting in precise microstructures [7]. Total doses for both normalization procedures are achieved with an accuracy of 10% from RBS data. Dose normalization will become much more precise when proton micromachining exposures are carried out with a state of the art 3.5 MV HVEE Singletron accelerator to be installed soon at the Research Centre for Nuclear Microscopy.

The microstructures in this paper are all produced in thin resist layers in order to prevent the "end of range" broadening of the beam envelope in the resist layer. These resist layers were applied on Si wafers using the spin coating technique. First the Si wafers are baked to remove moisture at the surface. The resist is then applied on the wafer and spun for typically 100 s at 1000 rpm; the exact conditions are dependent upon the resist type and desired thickness of the resist layer. Finally the sample is baked at about 95°C to harden the resist layer and to reduce stress.

After exposure the samples are developed in a chemical solution. The type of developer depends on the resist used, and the development time is a function of the thickness of the resist layer, the proton dose used and the temperature. The PMMA layers were developed using the procedure given elsewhere [8]. The other resists (AZ P4620, PMGI SF 23 and SU-8) were developed at room temperature using a common developer supplied by the manufacturers of the resists. Typical development times for these three resists are 3–7 min.

3. Results

The production of thick (>1 μm) PMMA resist layers on Si wafers is a rather complicated process [13]. We were able to produce 1–4 μm thick PMMA layers using the spin coating technique. In a 1 μm PMMA layer, structures 0.15 μm wide and 5 μm long were produced using a focused 2 MeV proton beam, with a spot size close to 1 μm^2, see Fig. 1. The beam dose per pixel was controlled using RBS normalization in each pixel.

During ion exposure of PMMA, scission of molecular chains occurs. These degraded polymer chains are removed by the developer, this results in

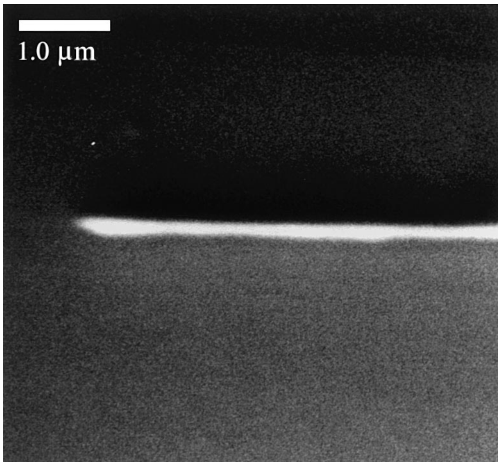

Fig. 1. SEM micrograph of a narrow line (150 nm) produced in a 1 μm thick layer of PMMA resist using a direct-write 2.0 MeV proton beam.

positive tone development. The typical dose range needed for complete exposure of PMMA is given in Table 1. The exact dose to expose PMMA resist depends on the proton energy used and the resist thickness. Using a proton energy of 600 keV requires only a dose of 60 nC/mm^2, which can be explained by the increasing *G* value of chain scission at lower energies. The *G* value is defined as the number of events, either chain scission or cross linking, per absorbed energy of 100 eV [14]. Test experiments with alpha beams at high doses indicated that the PMMA resist became insoluble due to effects of cross linking [15].

A 20 μm layer of AZ P4620 resist was applied on a Si wafer. The most suitable dose to irradiate AZ P4620 with 2.0 MeV protons is 150 nC/mm^2, see Table 1. Irradiation with protons gives rise to a combination of cross linking and chain scissioning [15]. Although this photo resist has a sufficient dose gap between positive and negative mode when used with photons, the dose gap is not large enough when used for proton micromachining, so this resist is not suitable for proton micromachining.

Fig. 2 shows microstructures produced with a 2.0 MeV proton beam in a spun layer of PMGI resist with a thickness of 12 μm. This pattern was exposed in an area of 400×400 μm^2. The top of Fig. 2 shows the smallest structures magnified. The narrowest walls on the right have a width of 1.5 μm. The proton dose per pixel was controlled using RBS normalization at each pixel. A proton dose of 300 nC/mm^2, see Table 1, was used to expose the PMGI at 2.0 MeV to make these detailed structures. However when applying the PMMA development procedure to the PMGI, a lower dose (100 nC/mm^2) was sufficient.

Fig. 3 shows two perpendicular walls produced in a 36 μm layer of SU-8 resist using 2.0 MeV protons. Because SU-8 is a negative resist, the structures which remain are those which have been cross linked by the proton beam. The proton dose used to expose the SU-8 was 22 nC/mm^2, the typical dose range for SU-8 exposure with protons is given in Table 1. As seen with the PMMA resist, a lower proton energy requires a lower dose, this is also valid for SU-8 because the *G* value of cross linking rises at lower energies. A uniform exposure was achieved using the repeat rapid scanning procedure.

It is clear from Fig. 3 that smooth walls perpendicular to each other with a well-defined intersection can be produced using proton micromachining. The walls appear to have a texture similar to walls produced in thick (2 mm) PMMA [9]. The main advantage of the walls produced in the thinner SU-8 layer is the fact that the end of

Table 1
Current status and dose requirements in proton micromachining

Resist	Type	Suitable for proton micromachining	Dose needed (nC/mm^2)	Smallest walls obtained (μm)	Highest aspect ratio (height/width)
PMMA	Positive	Yes	60–100	0.15	~ 100[a]
AZ P4620	Positive	No	150	–	–
PMGI	Positive	Yes	300	1.5	8–9
SU-8	Negative	Yes	10–40	1.5	24

[a] See [9].

range spread of the proton beam occurs in the supporting Si wafer and not in the resist layer.

To study the sensitivity of SU-8 and the end of range energy deposition of a proton beam in SU-8 resist a double exposure was performed in a 36 μm thick SU-8 layer. A set of 10 μm wide walls was exposed with a 2.0 MeV proton beam (dose 30 nC/mm^2). Perpendicular to these walls a 1.0 MeV proton beam was used to expose the SU-8 with a very low dose, 0.1 nC/mm^2. This dose is not sufficient to cross link enough molecules in the SU-8 layer at the surface, resulting in the removal of the SU-8 by the developer. As can be seen in Fig. 4, the end of range *G* value for cross linking with protons is higher and the SU-8 will not be affected by the developer, creating a bridge at 22 μm below the surface of the SU-8 layer.

Fig. 5 displays five cantilever structures produced in a single coated, 36 μm thick SU-8 layer applied on a Si wafer. Two exposures were performed with 1.0 and 2.0 MeV protons. The 1.0 MeV protons have a range of about 22 μm in the SU-8 layer and therefore this exposure was used to produce the cantilevers. A dose of 10 nC/mm^2 was used for this 1.0 MeV exposure. The supporting anchor was exposed with a dose of 35 nC/mm^2 using 2.0 MeV protons. The cantilevers have a length between 70 and 260 μm, a width of 20 μm and a height of 22 μm.

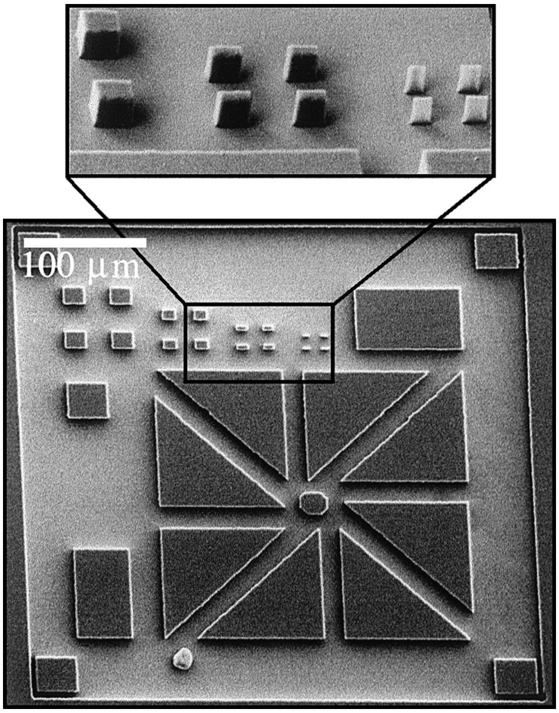

Fig. 2. SEM micrograph of structures produced in a 12 μm thick PMGI resist layer using a direct-write 2.0 MeV proton beam.

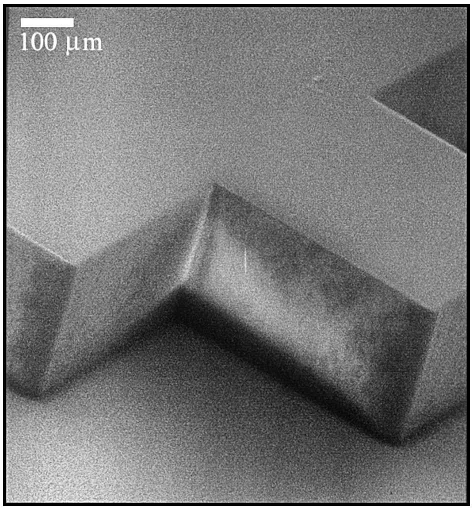

Fig. 3. SEM micrograph of straight walls produced in a 36 μm thick SU-8 layer using 2.0 MeV protons.

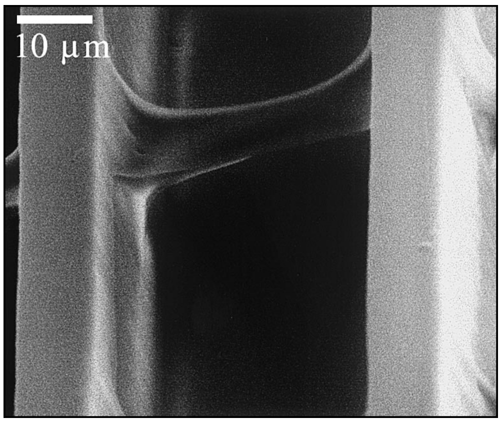

Fig. 4. SEM micrograph of a double layered structure showing the end of range energy deposition for a low dose exposure using 1.0 MeV protons. A 2.0 MeV exposure was used to produce the supporting walls.

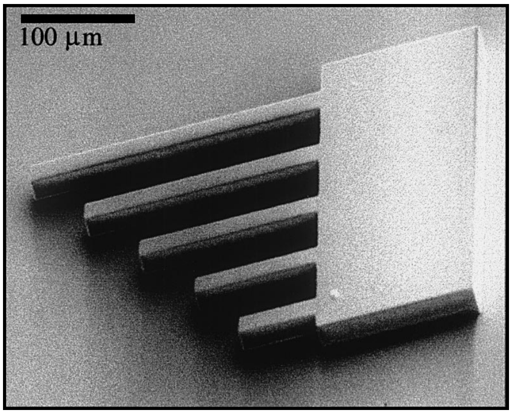

Fig. 5. SEM micrograph of a set of cantilevers produced in a 36 μm thick SU-8 layer. The suspended cantilevers were produced using a 1.0 MeV proton exposure and the anchor was exposed using 2.0 MeV protons.

Fig. 6 shows an example of an intricate multilevel structure made by proton micromachining. A 3D multilevel grid suspended by two anchors was assembled. This structure was produced using three different proton energies in one single layer of resist. In Fig. 6a an overview of the complete structure is shown. In the centre two anchors can be seen, produced using 2.0 MeV protons (dose 35 nC/mm^2). Fig. 6b shows the white dotted region in Fig. 6a and Fig. 6c is a schematic overview of the supported multilevel grid. Protons with an energy of 600 keV have a range of less than 10 μm in SU-8; this energy was used to produce the shallowest lines. The walls perpendicular to the first set were exposed with a 1.0 MeV proton beam; this resulted in 22 μm walls. This double layered grid was produced using an exposure of 10 nC/mm^2. The individual lines have a width of 5 μm and a spacing of 20 μm. The grid is suspended by the two anchors, 50×200 μm^2 each.

In a first attempt to produce high aspect ratio structures in SU-8, narrow walls were produced with a 2.2 MeV proton beam in a 36 μm SU-8 layer. The wall has a width of 1.5 μm, this corresponds to an aspect ratio of 24 which, to our knowledge is the highest aspect ratio published to date for SU-8. In Table 1 a summary is given for the current status of proton micromachining. The smallest walls produced and the highest aspect ratios obtained up to now are listed for PMMA, PMGI and SU-8 resist. It should be noted that these preliminary performances were achieved with an unstable proton beam, and that much improved performances from a more stable accelerator can be expected in the near future.

4. Conclusions

Proton micromachining using 2 MeV protons is able to produce 3D microstructures with complex

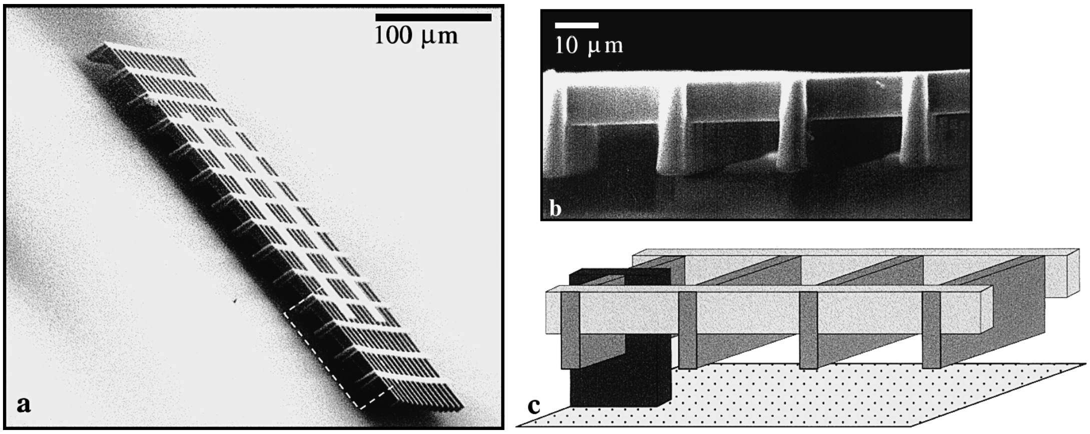

Fig. 6. SEM micrograph of a suspended multilevel grid produced in one 36 μm thick layer of SU-8 resist using three exposures at proton energies of 0.6, 1.0 and 2.0 MeV.

shapes and heights up to several tens of microns in positive resist such as PMMA and PMGI and in negative resist such as SU-8. It has been demonstrated that well-defined structures with straight walls can be produced using protons when a resist layer is applied on a substrate such that the end of range beam broadening occurs in the substrate.

In PMMA narrow walls of 150 nm have been produced. With the PMGI smooth walls with an aspect ratio of 9 have been produced. It is demonstrated that when an optimum proton dose is used in SU-8 the increased damage at the end of the proton range can produce structures below the surface. Finally it is shown that proton micromachining is able to produce multilevel structures in one single SU-8 layer of resist. This can be used to make cantilevers or multilevel grids which are only connected to the supporting Si wafer via small anchors.

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