



Proton beam micromachining on strippable aqueous base developable negative resist

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Abstract

Nowadays a significant amount of research effort is devoted to the development of technologies for the fabrication of microcomponents and microsystems worldwide. In certain applications of micromachining high aspect ratio (HAR) structures are required. However, the resist materials used in HAR technologies are usually not compatible with the IC fabrication, either because they cannot be stripped away or because they are developed in organic solvents. In the present work the application of a novel chemically amplified resist for proton beam micromachining is presented. The resist based on epoxy and polyhydroxystyrene polymers is developed in the IC standard aqueous developers. The exposed areas can be stripped away using conventional organic stripping solutions. In order to test the exposure dose sensitivity and the lateral resolution, various test structures were irradiated. Using this formulation 5–8 μm wide lines with aspect ratio 4–6 were resolved.

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1. Introduction

Proton Beam Micromachining (PBM), which is a novel direct-write process for the production of 3D microstructures [1–4], can be used to make multilevel structures in a single layer of resist by

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varying the ion energy. The interaction between the bombarding ions and the target material is mainly ionization and very few ions suffer high angle nuclear collisions, therefore structures made with PBM have smooth near vertical side walls. Due to the above mentioned properties of the PBM method a wide area of potential applications exists [5] in the fields of machines, sensors, actuator miniaturization and micro-electromechanical systems (MEMS).

The resists used in PBM so far are the positive, conventional, polymethyl methacrylate (PMMA) [2] and the negative, chemically amplified, SU-8 [6,7]. SU-8 is an epoxy based resist suitable also for LIGA and UV-LIGA processes [8], it offers good sensitivity, good process latitude, very high aspect ratio and therefore it dominates in the HAR micromachining applications.

SU-8 requires 30 nC/mm^2 dose for PBM irradiations [9]. Its crosslinking chemistry is based on the eight epoxy rings in the polymer chain, which provide a very dense three dimensional network in the presence of suitably activated photo acid generators (PAGs) which is very difficult to be stripped away after development. Thus, stripping has to be assisted with plasma processes or with special liquid removers. Moreover, the SU-8 developer is organic, propylene glycol methyl ether acetate (PGMEA) and thus environmentally non-friendly.

To overcome the SU-8 stripping limitations, design of a negative resist system where solubility change is not based solely on cross-linking but also on the differentiation of hydrophilicity between exposed and non-exposed areas is desirable. A new resist formulation, fulfilling the above specifications has been developed recently [10]. An aqueous base developable (IC standard aqueous developer (tetramethyl ammonium hydroxide – TMAH 0.26 N)) 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), has been proposed and successfully applied for UV-LIGA. This epoxy resist was also shown to have less or no swelling and reduced roughness problems compared to the pure epoxy novolac resists. In addition the exposed (crosslinked) areas can be stripped away using conventional organic strip-

ping solutions. This family of resists has been investigated for UV lithography at 365 nm giving $35 \mu\text{m}$ thick films with an aspect ratio of 7 for equal line-space structures 1:1 [11].

These resist materials were tested only in UV-LIGA and never in PBM technique. The aim of this work is to investigate the exposure dose sensitivity and the lateral resolution of this family of chemically amplified (CA) resists for PBM using the Debrecen Scanning Nuclear Microprobe facility. In the present study, the effect of ion dose and processing conditions in the case of several test structures is presented.

2. Experimental

All irradiations in this work have been performed on the nuclear microprobe facility at ATOMKI, Debrecen, Hungary [12–14]. The proton energy was 2 MeV. Beam currents of 5–60 pA were focused down to 2–3 μm spotsize. The scan size was typically 1000 μm .

The delivered dose was measured using the backscattering signals from the samples. First the beam chopper was calibrated to measure absolute charge. This was done on a compact Faraday cup as it was described elsewhere [15]. The error of this (chopper versus true charge) calibration was less than 1%. Then the yield of the backscattered ions was measured on the sample, while the beam chopper was still running. This way we established a (backscattering counts versus chopper) calibration factor for each sample. Finally when the product of the two calibration factors was calculated (resulting the backscattering counts versus true charge) the chopper was switched off; the delivered charge was proportional to the backscattered ion yield. A PIN detector array with the total area of 400 mm^2 was used to collect the backscattered ions. The same detectors were used for nuclear reaction analysis experiments in another work [16], here only the extremely high solid angle feature was exploited. The relatively poor energy resolution was not a problem because we integrated the whole spectrum for the charge collection. All of these counts in the spectrum came from the sample, the noise was first eliminated by a lower

level discriminator and we did not receive any counts when the beam was off (the detector array was well protected against light originated either from the vacuum chamber or from outside).

The above described PIN detector array acquired so high count rate on these samples, that it was possible to run “pixel normalization” mode, i.e. we collected the same amount of charge on each pixel. Thus, the current instability of the accelerator was eliminated, the scan speed was not constant but normalized by the beam charge.

The beam scanning was done using a National Instruments (NI) card (model 6711) and the new C++ version of the program IonScan, developed specifically for PBM applications called IonScan 3.x [17]. A home made electrostatic beam blanking system was used to eliminate unwanted beam exposure. The IonScan software produces the blanking signal via the NI card and then this blanking signal drives the home made amplifier that rises and eliminates the voltage on the plates. Both the rise time and fall time of the voltage on the plates are less than 1 μ s, which is negligible compared to the pixel dwell time (1–10 ms).

For the proton beam application two resist formulations were used. The first solution (*resist A*) consisted of 35% (w/w) total polymer concentration in ethyl(*S*)-(–)-lactate. The polymer was a mix of 83% (w/w) partially hydrogenated poly(4-hydroxy styrene) (PHS) with 8% degree of hydrogenation and 17% (w/w) epoxy novolac (EP). The used photoacid generator (PAG) was triphenyl sulfonium antimonite (TPS-SbF₆) 5% (w/w) with respect to the total polymer concentration. The second resist formulation (*resist B*) consisted 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. These relative compositions of both formulations were selected after lithographic performance optimisation for UV-LIGA.

The samples were spin-coated on a conventional spinner at 600 rpm (HeadWay Inc.) for 20 s on cleaned 3 in. Si wafers. Prior to spinning, silicon wafers were immersed in a solution of sul-

furic acid–hydrogen peroxide (80:20, v/v) for 30 min and washed with distilled water. The post apply bake (PAB) step was performed on a hot-plate at 95 °C for 45 min. Subsequently the samples were slowly cooled to room temperature on a warm metal plate; in order to reduce cracking caused by high temperature gradients between the silicon substrate and the resist due to their different expansion coefficients. The film thickness for resist A was measured to be 31.0 μ m and for resist B 30.0 μ m after the PAB step, on a calibrated Ambios XP-2 profilometer using low stylus force.

For the evaluation of the resolution and aspect ratio capabilities of the resists A and B suitable irradiation patterns were designed consisting of horizontal and vertical lines at various distances. In particular there were five lines of (a) 1 pixel width spaced by 20 pixels, (b) 3 pixels width spaced by 20 pixels and (c) 1 pixel width spaced by 50 pixels. This pattern was irradiated at 10 different doses on 4 samples of each formulation. The scan resolution was 1024 pixels, the scan size was 1000 μ m and therefore the developed line widths were thicker than the pixel size due to our beam spotsize. The samples were exposed at doses from 100 to 640 nC/mm². Top–down SEM images have been done from both resist formulations on all irradiations.

After the proton beam exposures, PEB (post exposure bake) was carried out at 100 °C or 110 °C for 8 min in order to study the effect of PEB. Subsequently the samples were slowly cooled down to room temperature.

The developer was tetramethyl ammonium hydroxide (TMAH 0.26 N) from Clariant (AZ-726 MIF). Finally the samples were rinsed in deionized water and dried with nitrogen. After the development the exposed patterns are easily stripped by immersing them in acetone in an ultrasonic bath for 30 min.

The evaluation of the final structures was performed in the Institute of Microelectronics, NCSR –“Demokritos” by a calibrated SEM (LEO 440).

3. Results

Representative results in case of PEB at 100 °C for 8 min are presented in Fig. 1. The resist A (Fig.

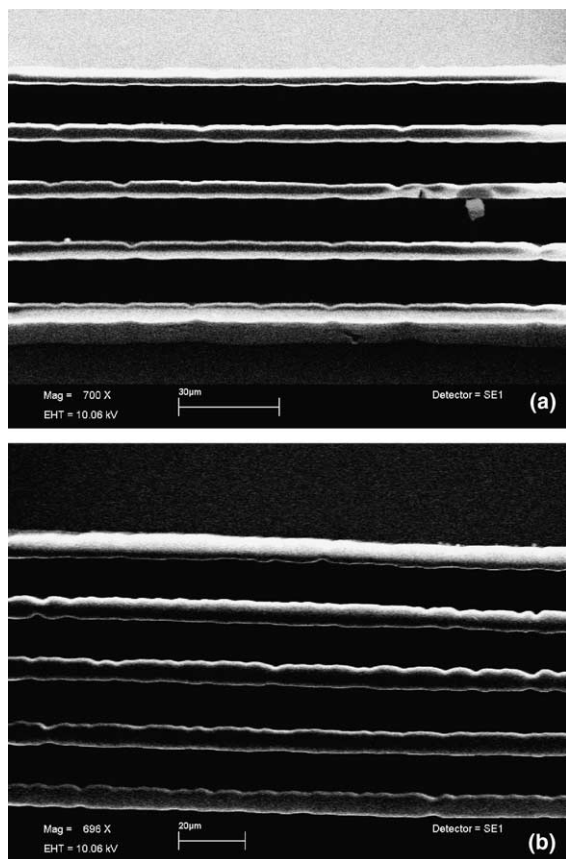


Fig. 1. Representative results in case of PEB at 100 °C for 8 min. (a) The resist A needs high dose (344 nC/mm^2) in order to resolve structures as small as $5 \mu\text{m}$. Moreover, this resist exhibits swelling and adhesion problems when it is developed for long times. (b) Resist B shows much better results at smaller exposure dose (238 nC/mm^2) without exhibiting adhesion problems.

1(a)) needs high dose (344 nC/mm^2) in order to resolve structures as small as $5 \mu\text{m}$. Moreover, this resist exhibits swelling and adhesion problems when it is developed for long times. On the other hand, resist B (Fig. 1(b)) shows much better results at smaller exposure dose (238 nC/mm^2) without exhibiting adhesion problems.

In Fig. 2 SEM images of both resists at almost the same exposure dose (116 nC/mm^2 for resist A and 125 nC/mm^2 for resist B) are presented; PEB was done at 110 °C for 8 min. Firstly, one can conclude that the increased temperature of PEB helps

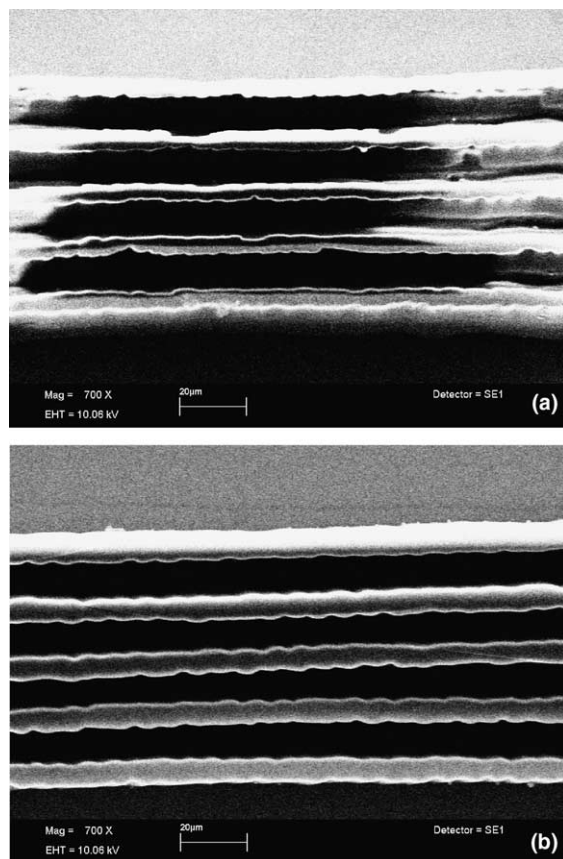


Fig. 2. SEM images of both resists at almost the same exposure dose (116 nC/mm^2 for resist A and 125 nC/mm^2 for resist B); PEB 110 °C for 8 min. The increased temperature of PEB helps significantly the crosslinking reaction (in both resists the necessary exposure dose was smaller for the 110 °C PEB than for the 100 °C PEB irradiations). The resist A did not fully develop, whereas the resist B is fully developed. Therefore the resist B is more sensitive and also needs less development time than resist A.

significantly the crosslinking reaction (in both resists the necessary exposure dose was smaller for the 110 °C PEB than for the 100 °C PEB irradiations). Secondly, the resist A did not fully develop, whereas the resist B is fully developed. Therefore the resist B is more sensitive and also needs less development time than resist A [11]. This is due to the higher hydrophilic properties of formulations B allowing shorter development times, which prevents adhesion problems.

4. Conclusions

Proton Beam Micromachining was performed at the Institute of Nuclear Research of the Hungarian Academy of Sciences on novel chemically amplified resists. The proposed resists are based on epoxy and polystyrene polymers and they are developed in the IC standard aqueous developers. The exposed areas can be stripped away using conventional organic stripping solutions, thus these materials are very promising for electroplating microstructures. In order to test the exposure dose sensitivity and the lateral resolution various test structures were irradiated for a wide exposure dose range. A PIN diode array was used for dose normalization. The detection efficiency for backscattered ions was so high that we were able to run pixel normalization.

Both tested formulations in the present work need about 125–238 nC/mm² dose. This is higher than that of the SU-8, but the tested formulations have the advantage of using IC industry developer solutions and easy stripping in acetone.

From the formulations examined, the resist formulation consisted of polymer mix of 78% (w/w) PHS with 12% degree of hydrogenation and 22% (w/w) EP and 1-(4-hydroxy-3-methylphenyl) tetrahydrothiophenium triflate (o-CS-triflate) 3% (w/w) as PAG provided the best patterning results. Using this formulation 5–8 μm wide lines with aspect ratio 4–6 were resolved.

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