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Micromachining using deep ion beam lithography

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Abstract

In recent years the process combining deep X-ray lithography with electroforming and micromoulding (i.e. LIGA), has become an important technique for the production of high aspect-ratio microstructures for the fabrication of micro-electro-mechanical systems (MEMS). The aim of this paper is to investigate the potential of high energy ion microbeams for carrying out similar micromachining, and in particular for overcoming the geometrical restrictions which are inherent in deep x-ray lithography. Using a scanned 2.0 MeV proton beam of approximately 1 micron diameter, we produced latent microstructures in high molecular weight PMMA resist. These resist microstructures were subsequently developed using a multi-component developer which is highly specific in the removal of exposed resist, while leaving unexposed or marginally exposed material unaffected. A suitable range of exposures has been established, and factors affecting the geometrical fidelity of the produced microstructure have been investigated. The relative advantages and limitations of this technique vis à vis deep X-ray lithography are discussed.

1. Introduction

In recent years the fabrication of sensor and actuator devices on the micro scale has become an area of considerable commercial interest, stimulating substantial research efforts in micromachining techniques. The LIGA process [1,2], combining deep X-ray lithography with electroplating and micromoulding, has emerged as an important technique for the fabrication of microstructures of large structural height (typically 300 to 500 microns), with lateral dimensions ranging from a few microns to hundreds of microns, and aspect-ratios up to 100. As a further refinement of the LIGA process, a sacrificial layer technique [3] enables metal structures which are partially or completely detached from the underlying substrate to be produced (e.g. cantilever beams, rotating gears, etc.). Despite its success, the LIGA process is hampered by the restricted geometry of the microstructures that can be fabricated (essentially prismatic), which is inherent in the masked Deep X-ray Lithography (DXL) technique which is the first step in LIGA. The objective our research has been to explore the use of a scanned high energy focused ion beam (Deep Ion Beam Lithography, DIBL) to perform similar micromachining work, which can potentially overcome the geometrical limitations of DXL. The potential advantages of DIBL lie, firstly, in the ability to orientate the resist surface at any angle to the beam direction, and secondly, in the well defined range and breadth of a beam of monoenergetic ions, as further discussed in Section 3.

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2. Procedure

All the exposures were performed using the nuclear microscope at the National University of Singapore [4], with a 2.0 MeV proton beam of approximately 1 micron diameter, and beam currents ranging from 10 to 400 pA. The standard Oxford Microbeams DAQ operating system for this machine enables a two dimensional map to be specified, determining the area over which the beam will be raster scanned. To facilitate comparison with early LIGA work [1], the resist used was the same commercially available (Röhm GS233) [1], mildly cross-linked, cast PMMA sheet of high molecular weight (mean of several 10^6). The density of this material is 1.19 g/cm^3, for which the measured range of 2.0 MeV protons is $\cong 63$ μm. In common with LIGA, development of the exposed resist followed the same basic procedure:

Development: one to two hours at 35 to 39°C, with mild agitation, in: 60% Diethylene Glycol Monobutyl Ether, 20% Morpholine, 5% Ethanolamine, 15% Water.

First rinse: 30 min at 35°C, with mild agitation, in: 80% Diethylene Glycol Monobutyl Ether, 20% Water.

Second rinse: 30 min at 35°C, with mild agitation, in water.

When used with high molecular weight PMMA this development procedure has been shown to be highly specific in removing exposed PMMA, while leaving unexposed and marginally exposed PMMA unaffected [5].

3. Results and discussion

Fig. 1a–d, shows resist microstructures created using DIBL, as described above. The cross pattern (a) reveals the limitations of the beam raster scanning system for lithographic applications. The surfaces parallel to the raster direction of the beam are sharply defined, but those perpendicular to the scanning direction have serrations representing the points at which the beam "jumps" across the bar. The upper surface of the bar shows slightly developed lines indicating a low exposure resulting from the transit of the beam across the bar. The Singapore nuclear microscope is primarily designed for analysis applications for which such limitations of the beam scanning system are irrelevant. Of course the implementation of a vector scanning and beam blanking system would completely eliminate such problems. Test patterns were written with varying exposure, and the most suitable range of exposures for 2.0 MeV protons was found to be 75 to 85 nC/mm^2. Exposures much below 70 nC/mm^2 resulted in incompletely removed resist, with exposures below 20 nC/mm^2 being almost completely undeveloped. Exposures much above 90 nC/mm^2 resulted in the formation of bubbles in the PMMA. Due to the peaking of the deposited energy density towards the end of the proton range any overexposure of the resist will be most pronounced close to the bottom of the developable depth of the material. Pot-hole like features are evident in the lower surface of the structure in Fig. 1b, indicative of bubble formation in mildly overexposed material. Higher levels of overexposure result in the increasing destruction of the PMMA resist. For an 80 nC/mm^2 exposure of 2.0 MeV protons the deposited energy density (calculated using TRIM [6]) at the surface of the resist is $D_S = 1.6$ kJ/cm^3, and it peaks at $D_{Pk} = 7.0$ kJ/cm^3 in the depth of the material. The deposited energy renders the resist developable by breaking up the polymer chains (chain scissions), progressively lowering the average molecular weight of the polymer as the deposited energy increases. For deep X-ray lithography it is found that the usable range of energy deposition is 4 kJ/cm^3 to 20 kJ/cm^3 [2]. Again, below this range incomplete development is observed, and above it the liberation of volatile chemical species produced by chain scissioning results in bubble formation. Hence the range of usable energy deposition for energetic protons is a factor of about 2.5 below that observed for DXL, but there is still a factor of approximately 5 between the highest and lowest usable energy depositions. Hence the ratio D_{Pk}/D_S is an important parameter which determines the latitude of exposure available, beyond which the surface resist will be underexposed or the deep resist overexposed. This ratio is plotted for both protons and deuterons as function of ion range in

[1] Röhm Gmbh, Darmstadt, Germany.

Fig. 2c, and shows that the $D_{Pk}/D_S < 5$ requirement is satisfied up to 100 μm depth, though exposure latitude is better for deuterons. The latitude of exposure will be considerably improved if the ion range is greater than the thickness of resist and the peak energy deposition occurs within a substrate material. Although not systematically investigated, the usable exposure range showed no significant dependence on the beam current I_b, or the beam scan rate. It is worth noting that range straggling is not a significant problem as energy deposition decreases rapidly beyond the peak in the energy deposition curve, and a highly specific development ensures the lower surface of a the developed resist void is quite flat, see Fig. 1a–d.

Further investigations focused on the production of narrow walls as these features make the greatest demands on the capabilities of the technique. Fig. 1c shows the thinnest wall which remained fully attached to the underlying resist, having a thickness of 5.2 μm at the upper surface, but due to the lateral deviation of ion trajectories, tapering to ≅ 1.4 μm near the point of contact. Barely visible in this micrograph are the remains of a thinner wall which has been undercut and broken away from the sidewall. Thin undercut walls can be produced if they are supported by thicker buttress walls as seen in Fig. 1d. The three undercut walls shown have depths and thickness which are respectively from left to right: (53 μm, 3.9 μm), (44 μm, 2.2 μm), and (20 μm,

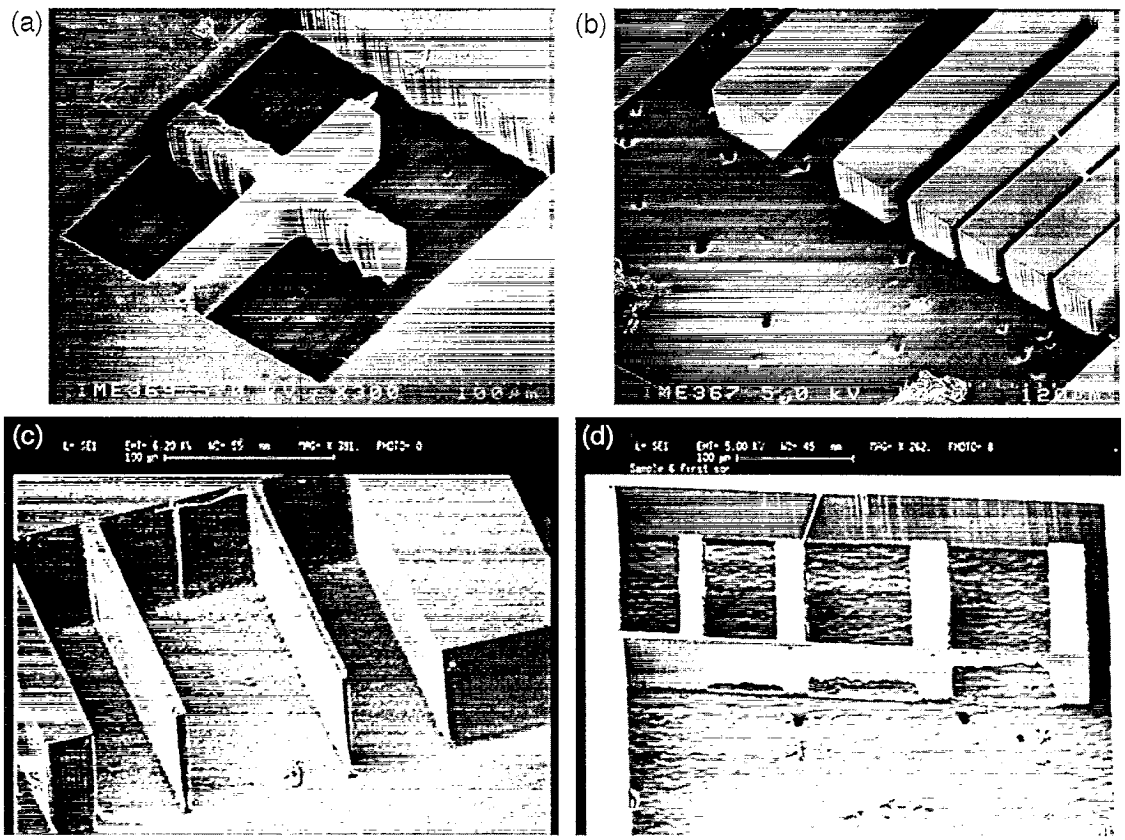

Fig. 1. SEM micrographs of test structures written in high molecular weight PMMA resist using a 2.0 MeV proton microbeam. (a) 250 × 250 μm square containing cross, exposure 73 nC/mm^2, $I_b \cong 200$ pA. (b) 500 × 500 μm square containing slotted channels, exposure 115 nC/mm^2, $I_b \cong 200$ pA. (c) Walls of varying thickness protruding from side of 400 × 400 μm square, exposure 88 nC/mm^2, $I_b \cong 10$ pA. (d) Thin undercut walls supported by thick buttress walls in 400 × 400 μm square, exposure 86 nC/mm^2, $I_b \cong 50$ pA.

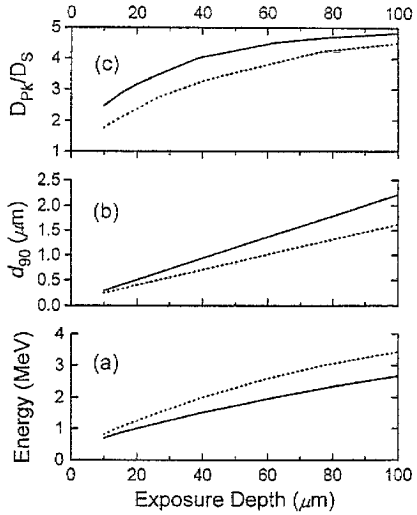

Fig. 2. Exposure parameters for protons (solid) and deuterons (dashed), plotted as a function of ion range: (a) ion energy; (b) figure of merit d_{90} for lateral deviation of ion trajectories; (c) ratio of deposited energy density D_{Pk}/D_S.

1.4 μm). Clearly the corresponding aspect-ratios are not as high as those acheivable with deep X-ray lithography.

It is clear that the ability to orientate the beam to the resist surface leads to greater geometrical freedom in the production of microstructures. However, there is also great scope for extending this geometrical freedom by exploiting the finite range of high energy ions. For example, following a resist exposure, the resist is not immediately developed, but rather a further layer of PMMA resist of suitable thickness is added to the surface and a second exposure made. Clearly this process could be repeated several times and terminated by a single development step in which all exposed volumes of the resist accessible to the developer are removed. If a metal substrate underlies the resist, this would permit the electroplating of metal structures of almost arbitrary geometrical complexity.

4. Theoretical considerations and simulations

Clearly, two important factors which influence the capabilities of this micromachining technique are, firstly, the range and distribution of energy deposition by the cloud of primary and secondary electrons surrounding each individual ion path, and secondly the deviation of individual ion trajectories from the ideal straight line path. In considering the first of these factors, the primary electrons are emitted with a distribution of energies which is limited kinematically to a maximum $T_e^{max} = (4m_e/M)T$, for ions of mass M and energy T, though most primary electrons have much less energy. The range of electrons of energy T_e (in eV) in a material of density ρ is reasonably approximated by the empirical relation $R(T_e) = CT_e^{\alpha}$, with $C = 5.2 \times 10^{-4}/\rho$, $\alpha = 1.67$, with R in nm, and ρ in g/cm^3. Using the density of the present resist, the primary electrons have a maximum range (corresponding to T_e^{max}) of $R_{max} = (164\ \text{nm})(T')^{\alpha}$, where T' is in MeV/u. Then as given by [7], the deposited energy density E at a radial distance r from the track of an ion of atomic number Z and velocity v, due to both primary and secondary electrons is $E(Z, v, r) \propto (Z/vr)^2(1 - r/R_{max})^{1/\alpha}$ for $r \leq R_{max}$. However, for the purposes of micromachining, for which the lateral dimensions of features are usually large by comparison with R_{max}, it is more appropriate to consider the distribution of deposited energy at a perpendicular distance d (into an unexposed region) from the boundary of a region uniformly exposed with energetic ions. Considering only isotopes of hydrogen, for which an energy dose $dE(T', r) \propto (1 - r/R_{max})^{1/\alpha}/(T'r^2)da$ is received at a point in the unexposed region due to ion tracks within an infinitesimally wide circular arc of radius r and area $da = 2r\cos^{-1}(d/r)dr$ lying within the exposed region, then the total energy received at this point by summing over all arcs up to radius R_{max}, is

$$D(d) \propto \frac{1}{T'}\int_d^{R_{max}} (1 - r/R_{max})^{1/\alpha} \frac{\cos^{-1}(d/r)}{r} dr.$$

This function, normalized to unity for protons of 1.0 MeV and $d = 1$ nm, is shown in Fig. 3. The energy deposition falls by a factor of approximately 100 at a distance of 300 nm for 2.0 MeV protons (or 4.0 MeV deuterons), and considering the great variation in solubility of the resist for a change in the deposited energy by even a factor of 10 [1], it is apparent that development of the resist will terminate at a distance less than 300 nm from the exposed region. Moreover the range of the electron cloud

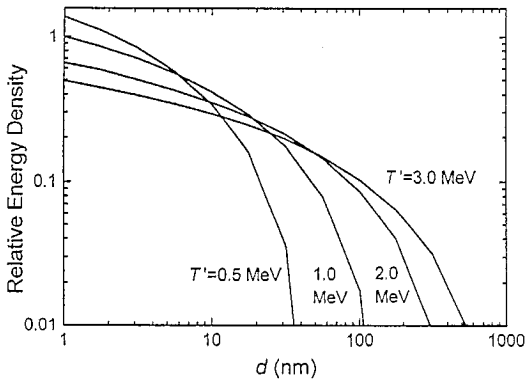

Fig. 3. Plot of calculated relative energy dose by primary and secondary electrons at a distance d beyond the boundary of a region uniformly exposed to energetic hydrogen isotopes. Curves have been normalized to unity for protons of 1.0 MeV and $d = 1$ nm.

decreases with increasing depth (as ion energy decreases), whereas the lateral deviation of ions trajectories increases with depth and soon dominates, hence the range of energy deposition by the electron cloud will only be of importance in a shallow resist of several microns thickness.

The second factor, namely the lateral deviation of ion trajectories was investigated using TRIM. Since this effect is dependent on the beam profile and the exposure level it is rather difficult to quantify, and therefore a figure of merit (d_{90}) has been employed, which is the 90% percentile perpendicular distance of displacement into the shadow region at the end of the ion range, for ions incident on the resist surface at the boundary of the exposed region. This figure of merit is plotted for both protons and deuterons as a function of exposed depth in PMMA resist in Fig. 2b. As might be expected, the deviation is less significant for deuterons.

5. Conclusions

A method of producing microstructures in high molecular weight PMMA resist using a scanned 2.0 MeV proton microbeam has been demonstrated, and a suitable range of exposures and development conditions have been established. The achievable aspect ratios are not as high as those obtainable with deep X-ray lithography, but deep ion beam lithography has a much greater capacity for the production of microstructures with a complex three dimensional geometry. The geometrical freedom of this technique can be further enhanced by the use of a multi-step process involving repeated exposures and additions of resist layers. Although only investigated theoretically, it seems clear that with regard to: lateral deviation of ion trajectories; the range of the primary and secondary electrons; and latitude of exposure; deep ion beam lithography is better performed with deuterons than with protons (if accelerating energy is sufficient for the required depth).

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References

[1] E.W. Becker et al., Microelectron. Eng. 4 (1986) 35.
[2] W. Ehrfeld, H. Lehr, Radiat. Phys. Chem. 45 (1995) 349.
[3] C. Burbaum et al., Sensors Actuators A25-27 (1991) 559.
[4] F. Watt et al., Nucl. Instr. and Meth. B 85 (1994) 708.
[5] V. Ghica and W. Glashauser, Verfahren fuer die spannungsfreie Entwicklung von bestrahlten Polymethylmethacrylat-Schichten, Offenlegungsschrift DE 3039110 Siemens AG, München.
[6] J. Biersack, L.G. Haggmark, Nucl. Instr. and Meth. 174 (1980) 257.
[7] R. Spohr, in: Ion Tracks in Microtechnology, ed. K. Bethge (Vieweg, Braunschweig, 1990).