Fabrication of micro-optical components in polymer using proton beam writing

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ABSTRACT
Proton beam writing is a new direct write lithographic technique that utilizes a high energy (MeV) submicron focused proton beam to machine or modify a material, usually a polymer. Structures made using p-beam writing have very smooth side walls, high aspect ratio, and a scale that can be easily matched to existing optical fiber technology (0.1 to 1000 µm). In this paper we demonstrate the use of proton beam writing for prototyping micro-optical components such as microlens arrays and gratings in positive and negative resist. The structures that are fabricated can be used for both rapid prototyping and for large scale replication with nanoimprint lithography.

Keywords: Keywords: proton beam writing, polymer, SU-8, PMMA, gratings, microlens array

1. INTRODUCTION
Polymeric materials offer several unique advantages over existing semiconductor and inorganic technologies (LiNbO₃, SiO₂ etc) for applications in microphotronics. Polymers can be easily coated on almost any substrate making it possible to easily integrate polymeric devices with existing silicon or non-silicon based technologies. The optical properties of polymers can be engineered to give the desired refractive index, loss, transparency or electro-optic coefficient. This makes it possible to manufacture both passive and active components such as high bandwidth modulators¹ and optical interconnects.² Furthermore, emerging lithographic technologies such as nanoimprint lithography (NIL)³ are well suited to low cost mass production in polymer. It is therefore important to have tools that can easily and rapidly prototype micro-optical structures in polymer. P-beam writing is a new lithographic technique that is well suited to producing such structures with a resolution down to 100 nm or better, and negligible proximity effects. In this paper we demonstrate the use of p-beam writing for producing microlens arrays, micro-Fresnel zone plates and gratings.

2. THE P-BEAM WRITING TECHNIQUE
P-Beam writing is a new lithographic technique that can be used to fabricate of micro-optical components. The main characteristic of the technique is the ability to rapidly prototype an arbitrary structure in polymer with a high degree of precision. The structures produced with the technique can have a high aspect ratio (Aspect ratio of 50 in SU-8⁴) and possess extremely low side wall roughness (2-3 nm).⁵ The smoothness of the side walls of p-beam written microstructures is a feature that is crucial for reducing scattering loss in optical components such as waveguides.⁶

The P-Beam writing technique utilizes MeV protons that are focused down routinely to approximately 100 nm or better. The fine proton probe is then magnetically scanned across a resist sample in a vector style allowing for almost any structure to be patterned.⁷ The proton beam can be blanked electrostatically and the sample moved via a Burleigh TSE-150HV Integral Encoder Stage over a total range of 1×1 inch. The optical encoder readout of the stage is accurate to within 20 nm allowing for step and repeat lithography and stitching over the whole stage travel distance in fields of up to 800 nm.

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P-beam writing is fundamentally different from the Focused Ion Beam (FIB) technique that utilizes keV heavy ions such as Ga to sputter material from a target. The P-Beam writing technique is used to chemically modify a material (crosslink or scission a polymer) to form a latent image in the sample that can be later developed into a structure. In this respect p-beam writing is more closely related to the e-beam writing technique. Unlike the keV electrons used in e-beam writing, the trajectory of an MeV proton in a material is hardly diverted by the target electrons due to the large mass difference between the protons and the target electrons ($m_p/m_e \approx 1800$). This results in structures that are highly orthogonal with respect to the beam axis. Furthermore, MeV protons have a very well defined range in a material (For Example $62\mu m$ in PMMA). This end of range can be used to directly modify the refractive index of a material at a given depth, determined by the proton energy. End of range modification has been successfully used previously to fabricate buried channel waveguides in polymers such as PMMA$^{8,9}$ and glass.$^{10}$

![Diagram of p-beam writing, FIB, and e-beam writing](image)

**Figure 1.** Comparison between p-beam writing, FIB and e-beam writing. This figure shows schematically the difference between the three techniques. The p-beam and e-beam images were simulated using SRIM$^{11}$ and CASINO$^{12}$ software packages respectively.

A schematic diagram comparing various projectile direct write lithographic and micromachining techniques is shown in figure 1. The proton and electron diagrams are simulated using the SRIM$^{11}$ and CASINO$^{12}$ monte carlo software packages respectively. One characteristic feature of electrons penetrating a material is the large amount of scattering that occurs with increasing depth. This beam volume, often approximated with a gaussian distribution, spreads laterally for a distance about equal to half the electron range. The beam spread of electrons places a fundamental limitation on the resolution that can be achieved in thick polymers. It is for this reason that high resolution structures fabricated using e-beam writing are typically done in thin layers. Secondary electrons generated from higher $Z$ substrates, such as Au layers for electroplating, can also pose a problem for producing high resolution closely spaced structures with e-beam writing. So called proximity effects occur when unwanted electron dose is deposited in a region during the irradiation of a neighboring feature. These problems can sometimes be corrected for in e-beam writing software,$^{13}$ or by depositing multiple layers.

When protons penetrate a material the maximum energy ($w_m$) that can be transferred to a free electron along the ion track is given by the classical formula$^{14}$
\[
\omega_m = \frac{2mc^2\beta^2}{1 - \beta^2}
\]  

where \( \beta \) is \( v/c \), \( c \) is the speed of light, \( m \) is the mass of the electron and \( v \) is the velocity of the proton. For 2 MeV protons, most of these electrons (delta rays) are emitted at 90° to the ion direction with energies less than 1 keV. The corresponding range of these delta rays are no more than several 10's of nanometers. For protons ranges significantly larger than the thickness of the polymer being irradiated, the energy deposited as a function of depth is approximately constant. Only as the ion approaches the end of range does the energy deposition rapidly increase. This feature means that a polymer patterned with a proton beam has an almost constant number of chain scissions (or cross links) with depth. This is quite different to lithographic techniques that use electromagnetic radiation (UV and X-ray) which have an exponentially decreasing dose with depth. Figure 2 shows a SRIM simulation of the energy deposited by 2 MeV protons in a 10 \( \mu \)m layer of PMMA coated on a Si substrate that has a 200 nm layer of gold deposited on the surface. The distribution of energy deposited with depth shows the almost linear energy deposition with depth in the polymer layer. An example of some test structures machined in a 30 \( \mu \)m layer of SU-8 photoresist spin coated on a Silicon wafer is shown in figure 3. The key feature that can be observed in these types of structures is the smoothness and orthogonality of the patterns, even over depths of several tens of microns.

**Figure 2.** SRIM2003 simulation of 2000 2 MeV protons incident on a 10 \( \mu \)m PMMA layer spin coated on a Silicon wafer with a 200 nm Au layer deposited on top. This figure shows the almost linear energy deposition with depth that can be achieved with MeV protons.

3. EXPERIMENTAL

All the irradiations presented in this paper were carried out using the p-beam writing facility at the Centre for Ion Beam Applications, National University of Singapore with a beam of 2 MeV protons. PMMA samples (950K molecular weight, 11% in anisol) were developed using a mixture of Isopropyl alcohol (IPA) and water in the ratio 3:7, and rinsed in deionized water. This developer was found to be more effective than the GG developer that we commonly use for larger structures and bulk PMMA. The lower viscosity of the IPA water developer results in a more effective removal of irradiated material, especially for sub-micron structures. The
Figure 3. Test structures showing the side wall smoothness and orthogonality that can be achieved using p-beam writing. These structures were fabricated in a 30 \( \mu \)m layer of SU-8 spin coated on a silicon wafer.

development time varied depending on the polymer layer thickness and the dose delivered to the sample. Grating structures were left in the developer for 30 min to properly remove all the irradiated material. The microlens arrays required less development time (approximately 10 min) because the irradiated areas were larger. SU-8 samples were developed in propylenglyglycol-monoethylether-acetate (PGMEA) for 90 seconds and then rinsed in deionized water. For samples where SU-8 was spin coated on a glass substrate, the glass was initially cleaned using a piranah etch in order to improve the adhesion between the glass and the photoresist. The proton dose used to expose the SU-8 and PMMA structures was 30nC/mm\(^2\) and 200 nC/mm\(^2\) respectively. The PMMA exposure dose used here is higher than the dose previously reported. It was found that the IPA-water developer requires a higher dose in order to get sufficient contrast between the irradiated and the non-irradiated regions.

4. RESULTS AND DISCUSSION

4.1. Micro-lens arrays

Several methods of fabricating microlens arrays using MeV protons in polymer have been reported in the literature. Ottevaere et al\(^{16}\) have been able to produce high quality microlens arrays by irradiating PMMA with MeV protons through a high aspect ratio non-contact metal mask. The molecular weight of the irradiated regions decreases due to the formation of free radicals, and MMA vapor is then diffused into the irradiated regions causing a lens-shaped volume expansion. This method has been successfully used to fabricate plastic microoptical interconnection modules for data communication applications.\(^2\) The requirement of having a high aspect ratio mask for making these structures means that the method does not lend itself to rapid prototyping of an arbitrary structure. For this a direct write method such as p-beam writing is a better choice as it allows one the flexibility to fabricate almost any structure. Furthermore, it becomes increasingly difficult to fabricate such high aspect ratio metallic masks for sub 100 nm resolutions.

Microlens arrays were fabricated using the thermal reflow process.\(^{17}\) The first microlens array example is shown in figure 4a. This array was fabricated in a 4 \( \mu \)m layer of PMMA spin coated on a 170 \( \mu \)m thick glass microscope coverslip. The regions surrounding the 20 \( \mu \)m diameter circular lenses was irradiated and subsequently developed to leave behind an array of pillars. The sample was then placed on a hot plate and heated well above the glass transition temperature of the polymer, at which point the polymer forms a spherical
microlens under surface tension. For reflow, the sample was placed on a hotplate at room temperature and then heated at a rate of approximately 5 degrees per minute. Upon reaching the desired temperature, the sample was maintained at this temperature for 20-30 minutes before being removed. Although several reflow temperatures were tried, the optimum reflow conditions was found occur at about 200°C. Knowing the thickness $L$, refractive index $n$ and diameter $D$ of the microlens, one can make an estimate of the focal length $f$ and radius of curvature $R_c$ using the equation\textsuperscript{17}

$$R_c = (n - 1)f = \frac{D^2}{4L}$$ (2)

Immersing the microlens array in a fluid like water, or covering the array with a UV curable resist that has a refractive index in between air and that of the lens material, allows one to further modify the focal length. The refractive index of the PMMA resist used in this study was measured to be 1.487 at 632.8 nm and 1.477 and 1550 nm using a Metricon 2010 prism coupler.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{(a) A 20 $\mu$m diameter microlens array fabricated in a 4 $\mu$m layer of PMMA spin coated on a glass microscope cover slip, (b) A Ni stamp produced by electroplating the same 4 $\mu$m thick microlens structure that was machined on a Si wafer, (c) Optical image of a 40 $\mu$m diameter lens array fabricated in a 12 $\mu$m layer of PMMA on Si, (d) SEM image of the same 12 $\mu$m thick structure.}
\end{figure}
Although P-Beam writing is a relatively fast technique (1500 s/mm$^2$), it still cannot be used practically for mass production of microstructures like lens arrays. For this it is desirable to first make a metallic master (stamp or mould) of the structure one wishes to fabricate using p-beam writing. The master is typically made by electroplating the original structure that is first defined in a polymer layer on a metal coated Si wafer. The master can then be used to nano-imprint several copies of the structure in a given polymer.

A second 4 $\mu$m PMMA microlens array was fabricated using the thermal reflow method, this time on a Si wafer with a metallic seed layer. After the lens array had been formed, a layer of 20 nm Cr and 200 nm Au was e-beam evaporated on the surface of the sample. The sample was then electroplated with Ni to form a metallic stamp shown in figure 4b. In future work, stamps made using this method will be used to fabricate microlens arrays in different polymers using nano-imprint lithography.

Images of more examples of thermal reflow PMMA microlens arrays are shown in figure 4c,d. These arrays were fabricated in a 12 $\mu$m PMMA layer that was coated on a Si wafer with a Cu metallic seed layer. The 12 $\mu$m PMMA thickness was achieved by spin coating a 4 $\mu$m layer and then baking the wafer at 180°C for a few minutes before repeating the coating step three times. Figure 4c shows an optical image of a 40 $\mu$m diameter microlens array on Cu (200 nm)/Si wafer. The focus of the microscope is shifted from the surface so that an image of the underlying metallic layer is observed in the lens. An SEM image of the same lens array is shown in figure 4d. The sample is tilted to 60° in order to see the spherical profile of the lens array.

### 4.2. Micro-Fresnel Zone Plates

Micro-Fresnel zone plates (MZP) are commonly used to focus X-rays from synchrotron sources, and may offer an alternative to CaF$_2$ optics for focusing extreme UV. For X-ray applications, MZP are typically made in metal like Au as they need to absorb x-rays in the 1-20 keV range. A typical plate can be several hundred microns in diameter, up to a few microns in thickness and the outer ring size as small as 100 nm. Here we demonstrate a MZP test structure micromachined in a 10 $\mu$m SU-8 layer on a Si substrate (figure 5). Such structures on Si can be used as polymer templates for electroplating a metallic replica that can be used directly as a MZP. MZP are usually fabricated on a thin Silicon nitride window to act as a support for the rings while still transmitting enough x-ray intensity. The resolution of the MZP depends on the width of the outer most ring. The negligible proximity effects and the ability to fabricate high aspect ratio, sub 100 nm closely spaced structures in thick polymer makes p-beam writing the ideal lithographic technique for the fabrication of MZP.

![Figure 5. Micro-Fresnel Zone plate test structures fabricated in a 10 $\mu$m SU-8 layer spin coated on a Si wafer.](image-url)
4.3. Gratings

Some examples of the type of gratings that can be fabricated using p-beam writing are shown in figure 6. Figure 6a,b shows a grating fabricated in an 800 nm layer of PMMA spin coated on a Si wafer with a Cr (20 nm)/Au (200 nm) seed layer. The PMMA lines are 700 nm wide and the spaces are 500 nm. The whole grating structure is 100 µm in length with a width of 30 µm. An identical grating was fabricated with a large cut away region along one edge. This cutaway enables for an SEM image to be taken looking along the edge of the grating showing the height of the structure (figure 6b). The extremely low line edge roughness can be easily observed in these images indicating that higher density lines and spaces are possible. The grating shown in figure 6c is fabricated in a 2 µm layer of PMMA on a Si wafer with a Cr (20 nm)/Au (200 nm) seed layer. This structure is the same size as the one shown in figure 6a,b except that it has a 590 nm line and 390 nm space. As the aspect ratio increases, surface tension effects that occur during chemical development can result in the structures collapsing unless the structures are anchored at both ends. Figure 6d shows an optical image of a grating that was fabricated in a 1 µm layer of SU-8 spin coated on a glass substrate.

Figure 6. (a) and (b) SEM images of a grating fabricated in a 800 nm layer of PMMA on Si. The lines are 700 nm wide and the spaces are 500 nm. (c) SEM image of a grating fabricated in a 2 µm layer of PMMA on Si. The lines are 590 nm the space is 390 nm. (d) Grating formed by irradiating a 1 µm layer of SU-8 on a glass substrate.
5. CONCLUSION

In this paper we have described a new three dimensional direct write lithographic technique that utilizes MeV protons for patterning resist materials. P-beam writing has a niche area in the fabrication of precise sub micron high aspect ratio structures in polymer. The extremely smooth side walls and orthogonality of the structures produced with p-beam writing are ideal for the fabrication of low loss and high quality micro-optical components. The technique can also be used to produce high quality metallic stamps and moulds for the replication of micro-optical components. P-beam writing has been used to demonstrate the fabrication of various micro-optical components for both refractive and diffractive applications including microlens arrays, diffraction gratings and micro-Fresnel zone plates. Future work will focus on producing micro-optical integrated devices for applications in bio-sensing, and the study of nano-imprint technology for replication in new polymer materials.

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