Final Report AOARD 07-4017

The Next Generation Focusing Lenses for Proton Beam Writing

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Aim of the project

1) Perform calculations to optimize a next generation spaced triplet magnetic quadrupole lens design.
2) Built the new lens system based on these calculations
3) Build a "basic" test beam line to evaluate the performance of these new magnetic quadrupole lenses.

1) New lens design:

Our lens calculations have shown that a system with 4 lenses will give a high system demagnification. The system demagnification will depend on the image distance used in the system see figure 1. With the new PI stage the image distance can be varied over a 20 mm range from 25 up to 45 mm from the last quardupole lens (Q4). This will give a system demagnification of 300 up to 600 in both x and y.

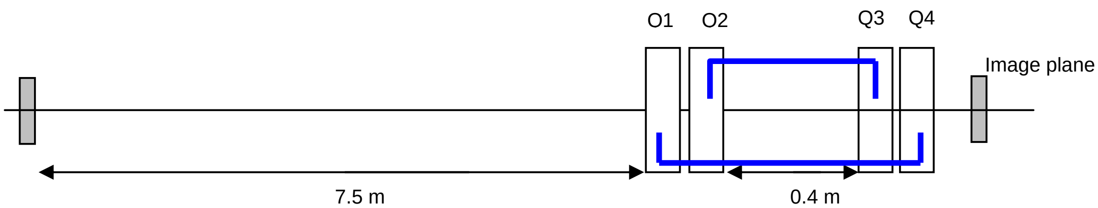

Figure 1 lens set-up for the new proton beam writing beam line at CIBA.

Beam optics calculations

Beam optics lens calculations have been performed, the results are shown in Figure 2 and Table 1. In Table 2 the characteristics for the current PBW beam line are given.

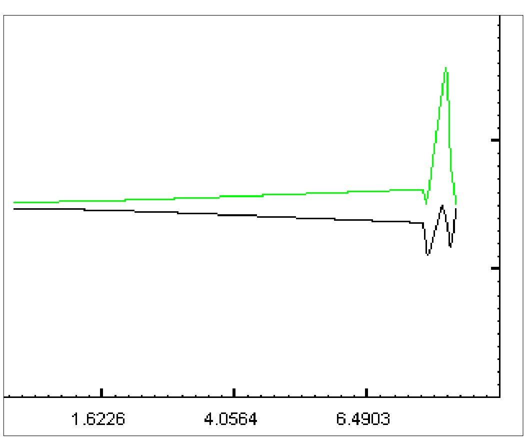

Figure 2 Calculated beam path in x and y traveling through the quadrupole lenses.

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14. ABSTRACT
The principal investigator (PI) has designed a new system for proton beam writing (PBW). The key characteristics are an improvement of the system demagnification of up to 8 and 30 in x and y respectively compared to commercially available systems from Oxford Microbeams. The target chamber is under construction and the system is expected to be assembled in October 2009. The PI has shown initial test on PBW for Ni and Au nanowire fabrication as well as ZnO nanowire fabrication. We have improved the resist development for nano wire template fabrication through optimization of resist which yielded higher resist contrast using the GG developer. A new resist material, TADEP has been investigated in combination with PBW and has shown details down to 110 nm. The PI has conducted 13 talks on Proton Beam Writing in which research was presented that was supported through this grant from AOARD.

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Table 1 Demagnifications and 2nd and 3rd order aberrations for several calculated systems.

<table>
<tr><th>working distance (m)</th><th>L1 (m)</th><th colspan="8">Non-Zero Aberration Coefficients* - units are microns and milliradians</th></tr>
<tr><th></th><th></th><th colspan="2">1st order - demag.</th><th colspan="2">2nd order - chrom.</th><th colspan="4">3rd order - spherical</th></tr>
<tr><th></th><th></th><th>$1/\langle x|x\rangle$</th><th>$1/\langle y|y\rangle$</th><th>$\langle x|x'\delta\rangle$</th><th>$\langle y|y'\delta\rangle$</th><th>$\langle x|x'^3\rangle$</th><th>$\langle x|x'y'^2\rangle$</th><th>$\langle y|y'^3\rangle$</th><th>$\langle y|x'^2y'\rangle$</th></tr>
<tr><td>0.03</td><td>0.4</td><td>457</td><td>457</td><td>-4374</td><td>-482</td><td>1018559</td><td>27003</td><td>7268</td><td>27003</td></tr>
<tr><td>0.03</td><td>0.6</td><td>622</td><td>622</td><td>-5295</td><td>-483</td><td>2038005</td><td>72576</td><td>12275</td><td>72576</td></tr>
<tr><td>0.05</td><td>0.4</td><td>315</td><td>315</td><td>-3274</td><td>-456</td><td>408631</td><td>19880</td><td>4606</td><td>19880</td></tr>
<tr><td>0.05</td><td>0.6</td><td>426</td><td>426</td><td>-3889</td><td>-464</td><td>788209</td><td>50075</td><td>8015</td><td>50075</td></tr>
</table>

Table 2 Demagnifications and 2nd and 3rd order aberrations for the existing PBW beam line in CIBA.

<table>
<tr><th>working distance (m)</th><th colspan="8">Non-Zero Abberation Coefficients* - units are microns and milliradians</th></tr>
<tr><th></th><th colspan="2">1st order - demag.</th><th colspan="2">2nd order - chrom.</th><th colspan="4">3rd order - spherical</th></tr>
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<tr><td>0.07</td><td>228</td><td>60</td><td>-382</td><td>976</td><td>2691</td><td>1159</td><td>-12619</td><td>-4447</td></tr>
</table>

Beam optics calculations have shown that this system has a scan size limitation of about 150 um. Beyond this the beam will get clipped in the beam pipe. Larger scan areas will have to be achieved either through stitching or stage scanning. In the case of stitching the beam would scan a field and the stage would step to a new position and a next field would be written. The alternative would be to use the scanning capabilities of the stage; this last option will have to be tested in the near future.

2) New chamber design.

In the chamber we will integrate a custom developed PI stage which has a travel of 20x20x20 mm^3 and a 1-2 nm closed loop positioning system and 5 nm step size. This newly developed stage is expected to be delivered to NUS in September 2009. At the same time the entrance of the new chamber has been re-engineered and the imaging distance will be reduced from 70 mm, currently available in the proton beam writing line in CIBA to 25-45 mm. This reduction will greatly improve the performance of the system, allowing higher system demagnifications. A sketch of the system is shown in figure 3.

Dose calibration:

The proton dose will be measured at the back of the target chamber, allowing for further reduction in working distance of the system. In between the microscope and stage we will mount:

1) a charge measuring faraday cup,
2) a PIN diode to count individual protons,
3) A hole to view the sample with the microscope
4) Space for future detectors.

A CEM (Channeltron Electron) detector for electron microscopy will be mounted on top of the stage to allow for easy beam focusing using proton beam induced secondary electrons.

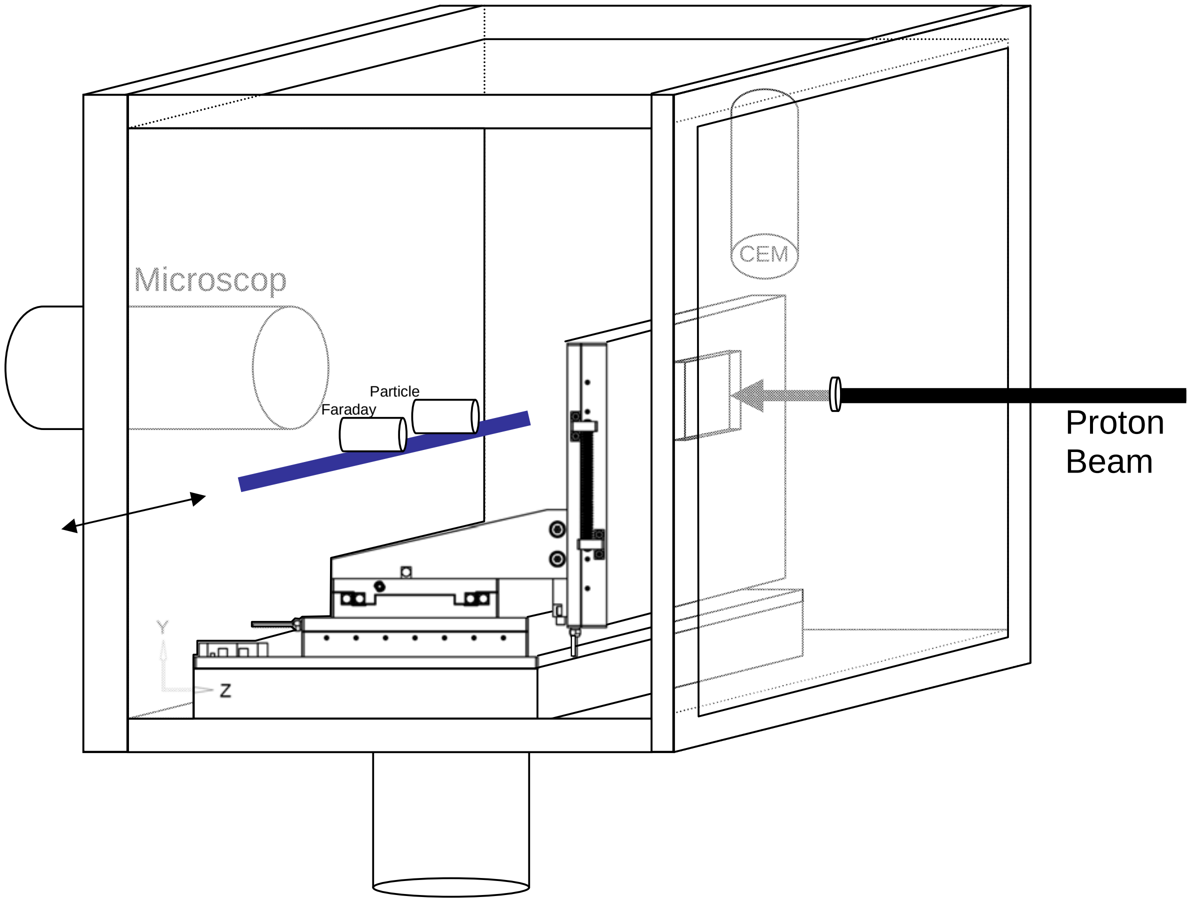

Figure 3 Sketch of the proton beam writing exposure system at CIBA currently under construction.

<u>3) Experimental achievements</u>

3A) Templated metallic nanowire growth on proton beam written templates

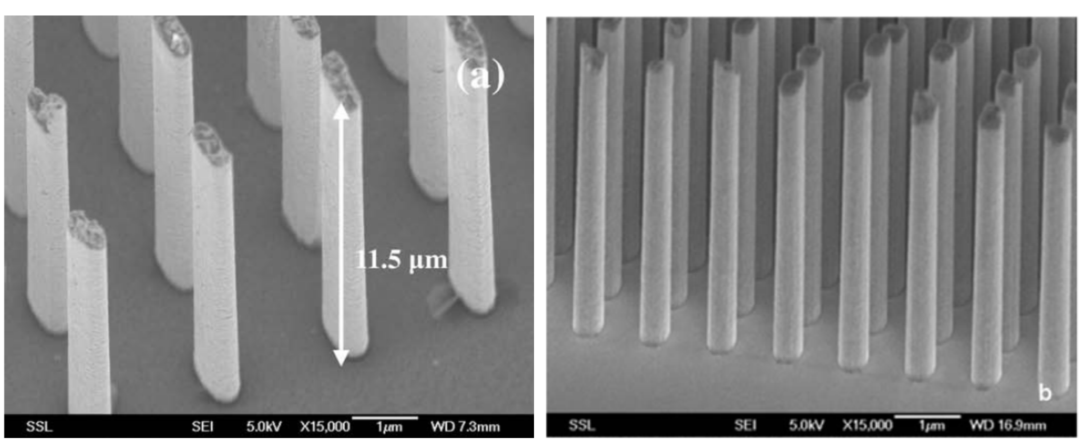

Figure 4 SEM micrograph of a) Au plated nanowires standing at 11.5 µm height. b) SEM micrograph of Ni plated nanowires standing at 5 µm height.

PBW with a finely focused 2 MeV beam was used to write holes in a matrix of thick PMMA. A G-G developer was used to develop the PMMA patterns. The G-G developer is a mixture of 60 vol% butoxyethoxyethanol, 20 vol% tetrahydro-oxazine, 15 vol% water and 5 vol% aminoethanol. The sample was developed for up to 40 min at a temperature of 20°C. After development, the sample was rinsed with DI water. In this work, we found that the combination of the G-G developer and low temperature helps to improve the sidewall quality of thick gold structures.

The gold electrolyte solution MICROFAB Au 100 was used for electroplating. During the process, the temperature of the water heat bath was kept at 60 °C and the plating current density was set at a constant value of 2.5 mA cm^{-2}. A magnetic stirrer was used to provide agitation throughout the plating process which improved uniformity of the solution. The deposition speed was about 1 μm of plated Au in every 5 min. When a sufficient thickness of Au had been deposited, the PMMA around the gold structures was removed by immersion in toluene at 40 °C The resulting Au nanowires are shown in Figure 4a [1].

PBW with a finely focused 2 MeV beam was used to write holes in a matrix of 40 x 40 with a spacing of 1 μm. The array of holes was written in a 10 μm thick PMMA film. After proton beam exposure the sample was developed in a IPA:DI mixture (7:3 by volume) for 10 min followed by a rinse in DI water. The Ni plating was performed in a Technotrans RD50 plating system and the thickness was aimed at half the height of the PMMA layer, resulting in pillars with a height of 5 μm. After plating the resist was removed in toluene at 40°C for 1 hr. The resulting Ni pillars are shown in Figure 4b [2].

3B) PMMA development

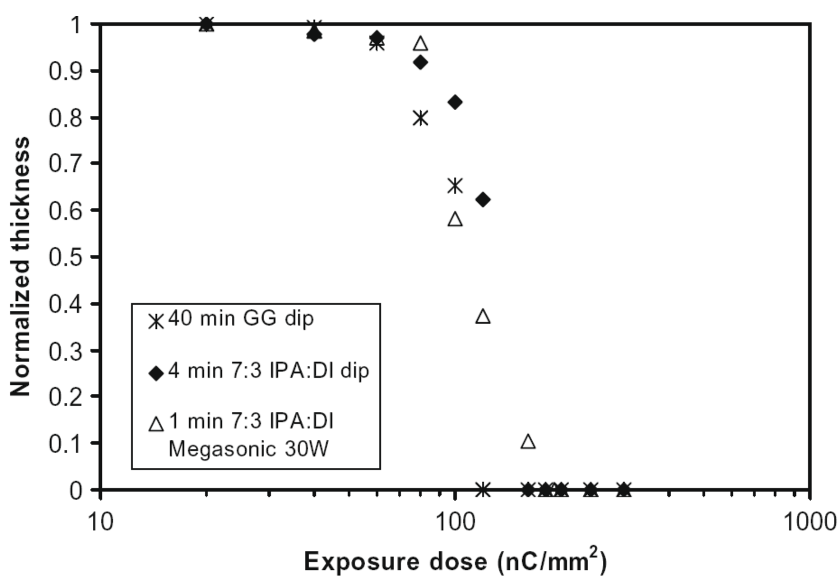

Figure 5 Contrast curves of dip development for 40 min in GG-developer, and 4 min in 7:3 IPA/Water. The third curve shows megasonic assisted development (30W) for 1 min in 7:3 IPA/Water.

We also investigated the influence of different developers on the development in PBW exposed PMMA. Here we show for the first time that the GG-developer is capable of developing 127 nm wide, high aspect ratio structures in proton irradiated PMMA. The use of GG-developer for dip development of PMMA gives the highest contrast and best sensitivity; 8.0 and 120 nC/mm^2, respectively. For the 7:3 IPA/water developer system a contrast of 6.1 and 3.1 was obtained for dip development and megasonic assisted development (30 W), respectively, see figure 5. Feature sizes down to the 120 nm level were obtained. With a smaller beam spot size and the optimized development procedures for MeV proton beam exposed PMMA a further reduction in feature sizes is expected [3].

3C) ZnO nano wires on PMMA templates

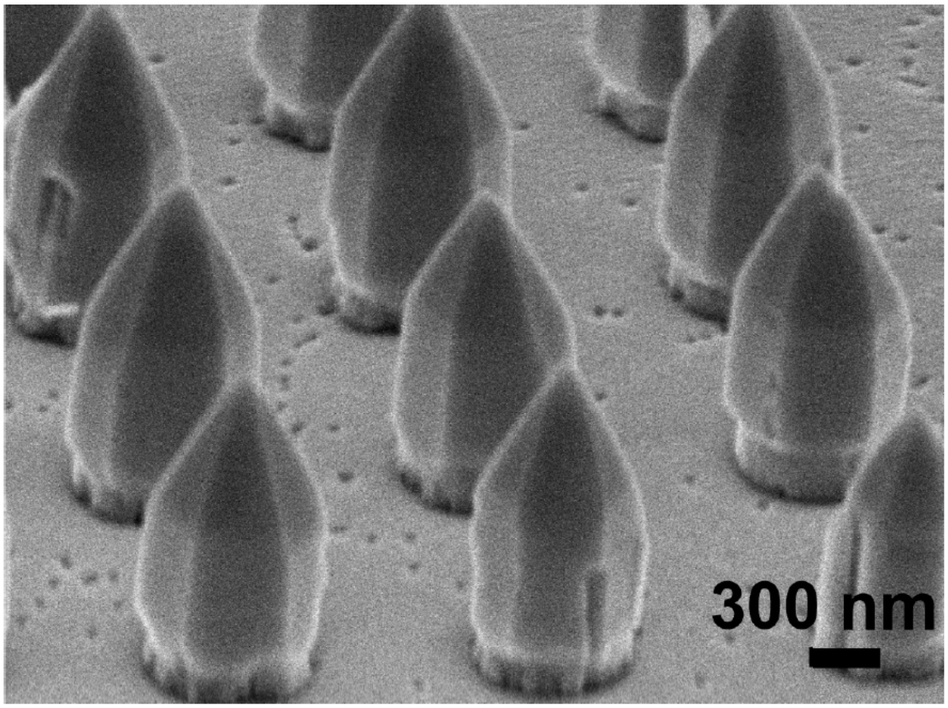

Figure 6 SEM birds-eye view image of the ZnO nanorod arrays selectively grown using a patterned PMMA template.

In this work we have demonstrated the controlled growth of ZnO nanorod arrays using the hydrothermal growth method grown on GaN/sapphire substrates. The PMMA template on which the nanorods were grown was patterned by proton beam writing. The highly ordered vertical aligned nanorods have uniform hexagonal structure with a diameter of around 400 nm, dictated by the template pattern feature size. The observed height of the nanorods was about 1.5 μm. After annealing, the nanorod arrays made using this technique are highly crystalline and are of excellent optical quality, see Figure 6. We have shown that this fabrication process offers a simple and efficient method to fabricate ordered nano arrays of controlled dimensions, and has high potential in the development of vertical nanorod devices [4].

3D) TADEP a new resist material for PBW

In SU-8 high aspect ratio nano structures have been produced with PBW but the usefulness is limited because the SU-8 can not be removed after Ni electroplating. Therefore we have explored the a newly developed negative resist material in collaboration with I Raptis from the Institute of Microelectronics, NCSR ‘‘Demokritos’’, Athens, Greece. PBW was explored and optimized for the patterning of an aqueous base developable negative chemically amplified resist (TADEP). By employing PBW on 2.0μm thick TADEP, patterns with 110 nm line width and an aspect ratio of 18 were resolved, see Figure 7. Initial test show that this resist can be easier removed after Ni electroplating compared with SU-8.

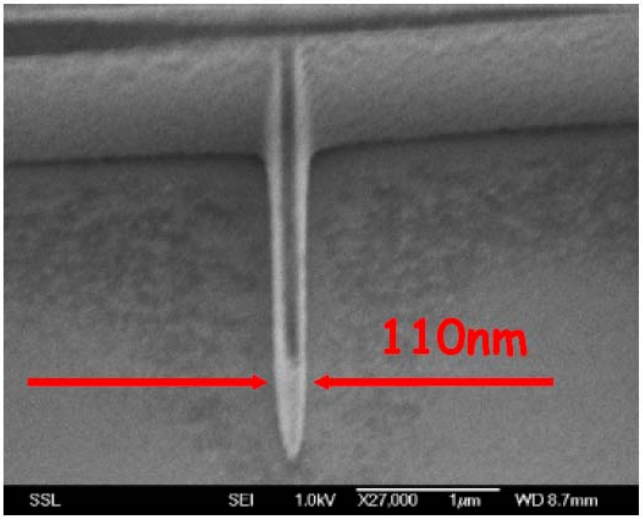

Figure 7 SEM images from the PBW on 2-μm-thick TADEP resist on Si.

4) Published and presented work related to our AOARD 07-4017 project.

Our project AOARD 07-4017 has resulted in five scientific publications in the area templated nanowire growth or closely related to this research [2,3,4,5,6]. One paper on the fabrication of Au X-ray masks for LIGA exposure is closely related to this work. Here Au nano wire structures are fabricated in a similar way as proposed for the templated nanowire growth [1].
During the reporting period the PI has also performed research which is related to the AOARD 06-4004 project "Studies into sub 100 nm resists for proton beam writing". This work resulted in 2 publications in collaboration with [7, 8] and one publication in CIBA [9]. These three papers are also of importance to this project since they deal with either new resists or different approaches to PBW nanofabrication which is crucial for the future work on integration of templated nanowires into functional devices. This is the main goal of our current project on "Next generation proton beam writing a platform technology for nanowire integration" AOARD 09-4020.
In 2007-2009 Jeroen van Kan has conducted 13 guest lectures and conference seminars on proton beam writing. At all these seminars work was presented that was partially supported by US air force grants obtained by the PI:

1. Invited Oral presentation: 2009 July at the 5th Singapore – China joint Symposium on Research Frontiers in Physics, Singapore
2. **Invited Oral presentation: 2009** March at the American Physical Society Meeting, Pittsburgh, USA.
3. Invited Oral presentation: 2009 January at the India-Singapore Joint Physics Symposium, Calcutta, India.
4. Invited Oral presentation: 2008 August at the Workshop on the Frontiers of Nano-Science & Nano-technology, Nanocore& NUSNNI, NUS, Singapore.
5. **Invited Oral presentation: 2008** June at the 25th Conference of Photopolymer Science and Technology Photopolymer Conference, Chiba, Japan, **all expenses paid**.
6. **Invited Oral presentation: 2007** at the 18th International Conference on Ion Beam Analysis, Hyderabad India.
7. Oral presentation: January 2008 at the SMART meeting, Singapore. Title A nano-fluidic lab on-a-chip platform for DNA studies
8. Oral presentation: 2008 at SPIE Advanced Lithography, section Emerging Lithographic Technologies, San Jose (CA) USA.
9. Oral presentation: 2007 at ICMAT, Singapore

10 **Cambridge University, December 2008, expenses paid in Europe.**
11 University of Twente, The Netherlands, September 2008
12 Shibaura Institute of Technology, Tokyo, Japan, June 2008, all expenses paid.
13 **Berkeley Lab, California, USA 2008.**

5) Summary

We have designed a new system for proton beam writing. The key characteristics are an improvement of the system demagnification of up to 8 and 30 in x and y respectively compared to commercially available systems from Oxford Microbeams. The target chamber is under construction at the moment and the system is expected to be assembled in October 2009.

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