

The characterisation of optical elements that approach the diffraction limit of light.

Abstract

In this investigation, I examine the validity of the Newton's prism experiment on a micro scale, using PDMS ((poly)dimethylsiloxane) as the material for the optical elements, such as the Newton's prism and light jetting structures. I use focused ion beam milling to produce a refractive prism that is a few micrometres in length (1 micrometre or micron is a thousandth the length of a millimetre). From this I also observe the behaviour of light through a prism, which approaches the diffraction limit.

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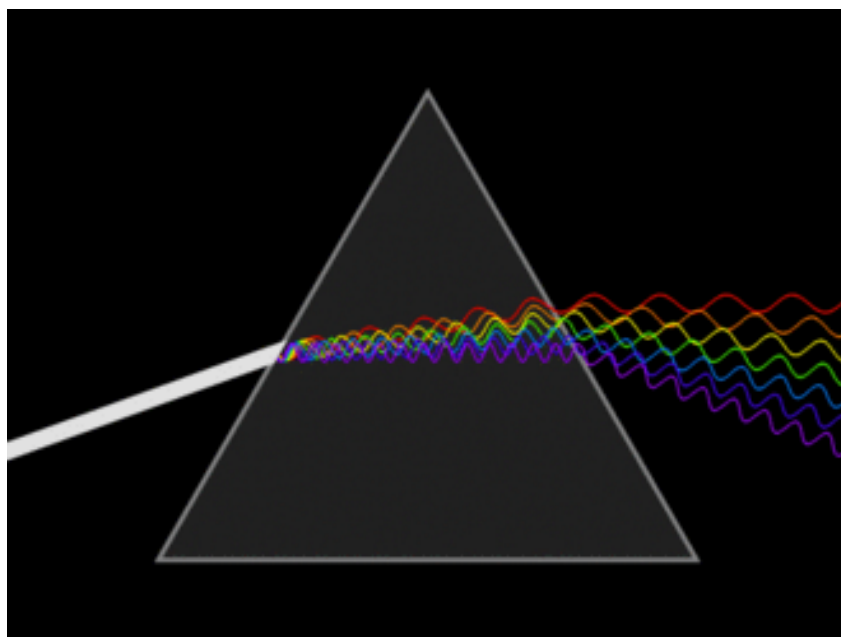
1. Introduction

How small can optical devices be made (e.g. for optical computing) and what effect does changing the size of the optical device have on the refraction pattern?

In this experiment, I am using optical elements manufactured from PDMS ((poly)dimethylsiloxane) to refract light. Although it is known that PDMS and other similar materials will refract light into a spectrum, this phenomenon has never been investigated thoroughly on a micro scale and so I am unsure how (or if) the same results will be observed on such a small scale. Refraction occurs because of the change in the refractive index between two substances. Light travels slower in optically denser substances. If light crosses the boundary between two substances of different refractive indexes at an angle other than the normal, light will refract and change direction. This phenomenon has been extensively investigated (in Snell's law for example), however I hope to determine whether conducting this experiment on a micro scale, near the diffraction limit of light, would have any effect on the refraction pattern of light. My Goal was to produce optical microstructures in PDMS and test their optical behaviour, particularly when their dimensions approach the diffraction limit.

2. Theory of prism design and method of milling structures

2.1 The refractive prism (or Newton's prism) can be used to diffract visible light into its full spectrum. This is due to the incident angle that the light is directed at the prism. I have decided to use a refractive prism because it has been shown that, if a correct material is chosen then, it refracts light very well. I produced an equilateral prism because it was the simplest to mill and there was no need to specify the angles particularly because I could direct the angle of incidence at the angle I specified. The relationship between the size of the prism and the refraction pattern has not been extensively investigated and is one of the things that I will be researching.



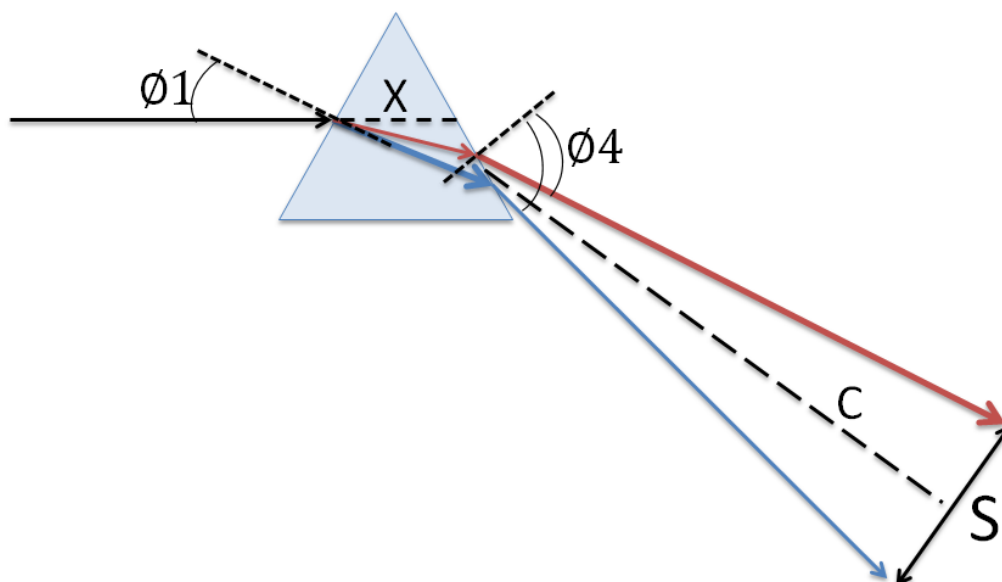
Refractive prism

Firstly, before I started milling the structures, the dimensions of the structures and the distances of the structures from each other had to be calculated. To do this, I constructed a preliminary design of the setup of the experiment and calculated the angles of incidence and refraction and how wide and far away the screen would have to be to display the full spectrum. The two wavelengths at opposite ends

of the spectrum (blue light at 300nm and red light at 800nm) would refract at different angles when emerging from the prism. The refractive index for each wavelength had to be known to calculate the angle of refraction of the two different components of visible light when emerging from the prism.

2.2 The refractive index of a substance is different for different wavelengths. This is because when light crosses the air-substance boundary it changes speed, causing it to bend (refract). The amount by which the light bends can be calculated using Snell's law, which states that for an incident substance with refractive index n_1 and a refractive substance with index n_2 , the angle by which the light will bends from the normal line (r) is equal to $\sin^{-1}\left(\frac{n_1}{n_2} \sin i\right)$, where i is the incident angle. The change in speed of light of a shorter wavelength is greater than the change in speed of light of a shorter wavelength, so refraction is greater since the refractive index of the substance is equal to $\frac{C}{C_s}$, where C is the speed of light incident to the substance and C_s is the speed of light in the substance. Hence the refractive index of substances is greater for blue light than for red light. To calculate the refractive index for each wavelength, I obtained a graph of refractive index vs. wavelength for the substance I was using. I then converted the graph into raw data and calculated the refractive index for light of wavelength 300nm (blue light) and 800nm (red light). I used these values because they are at opposite ends of the visible light spectrum. I only calculated the refractive index for these two values because I needed to know the overall dispersion of light in the substance but I did not need to know how much each individual colour would refract by. By calculating the dispersion, I was able to determine how far away the screen would need to be so that I could view a full spectrum of a particular width. This was necessary in order to decide whether or not the system was practical. If the prism-screen distance were too large compared to the spectrum width, then I would have to reconfigure the design so that a spectrum width with a reasonable prism-screen distance could be achieved.

2.3



$$\sin^{-1}\left[\frac{n_2}{n_1} \sin\left(\underbrace{60 - \sin^{-1}\left[\frac{n_1}{n_2} \sin \phi_1\right]}_{\phi_2}\right)\right] = \phi_4$$

n_1 = Refractive index of the incident substance (air) n_2 = Refractive index of refractive substance (PDMS)

θ_1 is the angle of the incident ray θ_2 is the angle of refraction of the ray from θ_1

θ_3 is the incident angle at the prism-air boundary θ_4 is the angle of refraction from θ_3

I formed a formula to enable me to calculate the angle of refraction when emerging from the prism in one step. The formula is made up of the refractive angles throughout the boundaries of the prism. I could therefore work out the minimum separation distance if the beams emerged from the prism at the same point.

$$S = \frac{c}{2.7} + \frac{x}{20}$$

S=Spectrum width C=Prism-screen distance X=Prism width from the point of contact between the incident beam and the prism

With this formula, I could work out the spectrum width at particular distances from the prism. I then worked out how far away the prism would need to be to achieve a certain spectrum width. I worked out the distance for a spectrum width of 21 micrometres. This was because there are 7 colours in a visible light spectrum. Each colour would be 3 micrometres wide, which was close to the resolution of the microscope. This way, I could observe each colour in detail on the smallest scale possible.

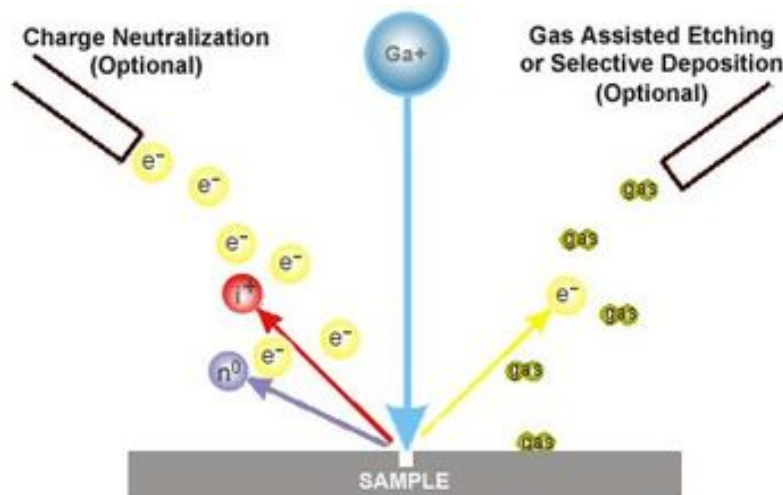
To construct this formula I had to find the relationship between the size of the prism and the effect it would have on the width of the spectrum. During my calculations I found an interesting relationship between the prism width and the dispersion of light within the prism. The equation shows that the dispersion of light within the prism is 5 percent of the prism width from where the incident beam first touches the prism. When the equation is applied to the prism in the experiment, it shows that the prism width increases the spectrum width by 150 nm. This affects the spectrum width by a negligible amount, since the shortest wavelength I am observing is twice this size and the resolution of the microscope is approximately 20 times larger. However, it shows that if a substantially larger prism was used, the prism width could affect the spectrum width by a significant amount e.g. a 10cm wide prism would increase the spectrum width by 5mm.

2.4 The jetting structure is responsible for producing the beam of light used in the experiment. Light shines through the flat side of the structure and is refracted by the curved edges. This causes the light to converge at particular points. The intense beam of light forms through the points of convergence between the two refracted beams on either side. The depth of the curve affects the length of the beam. Deeper curves produce a longer beam. The length separating the endpoint of the two curves affects the width of the beam. A smaller separation length will produce a thinner beam. I decided to use a structure that would produce a long thin beam. This was so that the length at which I could place the

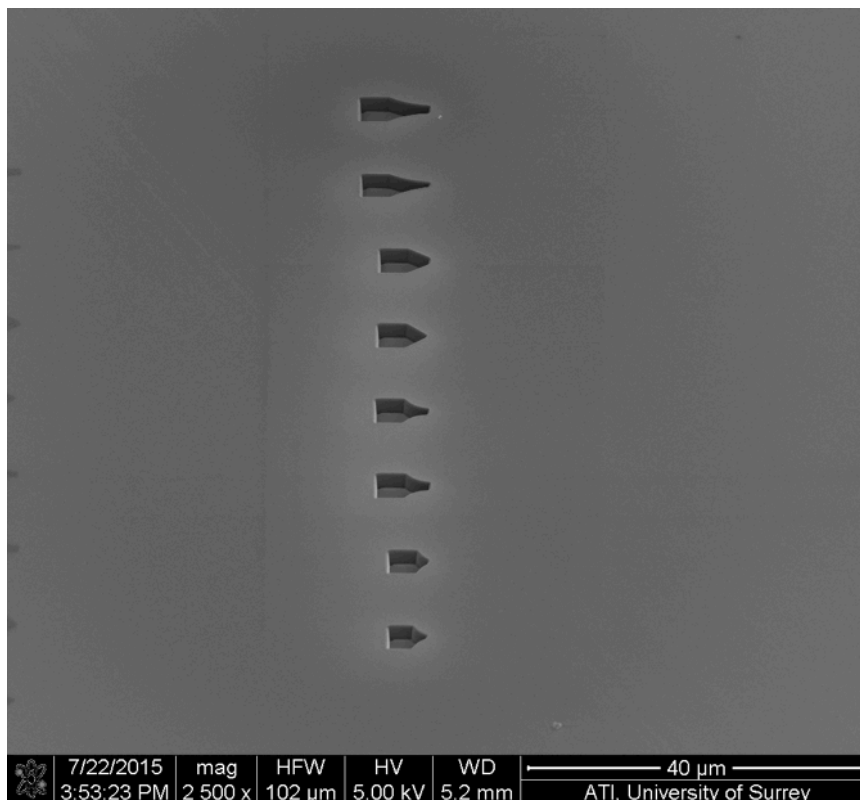
structure from the prism would not be a limiting factor and a thin beam would mean that I would be able to measure the angle of the refracted light more accurately.

To produce our optical elements, I used focused ion beams to mill out a particular design onto a section of a silicon wafer. I used silicon because it is widely distributed and easily available to obtain as wafers, which can range in thickness from a few millimetres to a few centimetres. They are practically 100% pure and nearly defect free. By adding atoms of different materials in precise amounts to the molten silicon, the crystallinity of the finished product can be specified. A seed crystal (from which a larger crystal can be grown from) is then added to the molten silicon and can be drawn up, forming a cylindrical shape known as a boule. The boule is then sliced in thin layers to form the silicon wafers. Silicon wafers are widely used to produce electrical elements due to their semi conductive properties. Silicon can be quite easily milled using FIB and so I am using it as the substrate for the optical elements to be milled in.

2.5 Focus ion milling is a technique used to manufacture different structures on a micro or even nano scale. It involves directing a beam of ions onto a section of the sample. As the ions make contact with the sample, material is removed, meaning that a small section of the sample has been carved out. By controlling the dose and duration of the beam at a particular point, the depth of material that is removed from the sample can be specified. At high beam currents, more material is removed and so the pattern is milled more deeply. At low beam currents, very little material is removed and instead of milling, the machine can be used as a microscope in a similar way to an SEM (Scanning Electron Microscope), where the sputtered ions or secondary electrons are collected to form an image. Sensors can measure the angle at which the ions or secondary electrons are emitted from the sample and can also measure the intensity of the emitted particles. This information is then converted into an image. An advantage of this image technique is that the image formed is 3D, whilst other microscopes, such as TEMs (Transition Electron Microscope) can only form a 2D image and multiple images of different layers need to be compiled to form a 3D image. This means that SEMs can be used to study tiny structures in detail such as microorganisms or nano devices. However, some disadvantages to SEMs and FIBs are that a SEM has a lower resolution than a TEM and therefore there is a greater restriction to the size of things, which can be viewed using an SEM. Although FIBs can be used as an imaging device, it has the limitation of undesired sputtering. Ions are much larger and heavier than electrons (approximately 130,000 heavier), which means that when FIB is used for imaging it also sputters material. Therefore, when imaging the substrate it may also become damaged as material is removed. In light of this, when I were imaging the sample, I primarily used the SEM to image the sample before milling it using the FIB. This enabled us to reduce the amount of undesired sputtering. Although the greatest intensity of sputtering is where the beam is directed, there is also a small amount of sputtering around the area of desired sputtering. This undesired sputtering is not very significant, however it can severely damage the structures if the FIB is used for imaging over a long period of time. It can particularly causes severe damage to areas being very lightly milled, as the depth of desired sputtering is very small, undesired sputtering can also lead to the whole area of the substrate being milled to the same depth. Subsequently, it is most important to control the length of FIB imaging when milling structures to a shallow depth. Fortunately, undesired sputtering was not a significant issue in this experiment because I carefully controlled the length of time I used to image the sample and I also milled the structures to a deep depth, so the effect of undesired sputtering would be very minimal.



FIB (Focused Ion Beams)

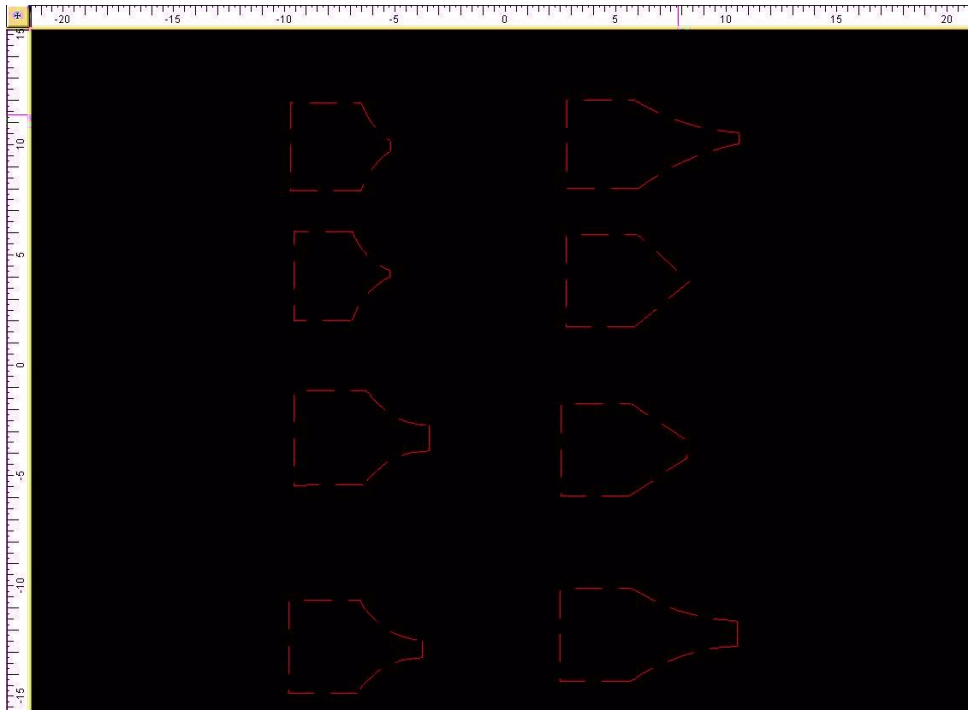


Milled jetting structures

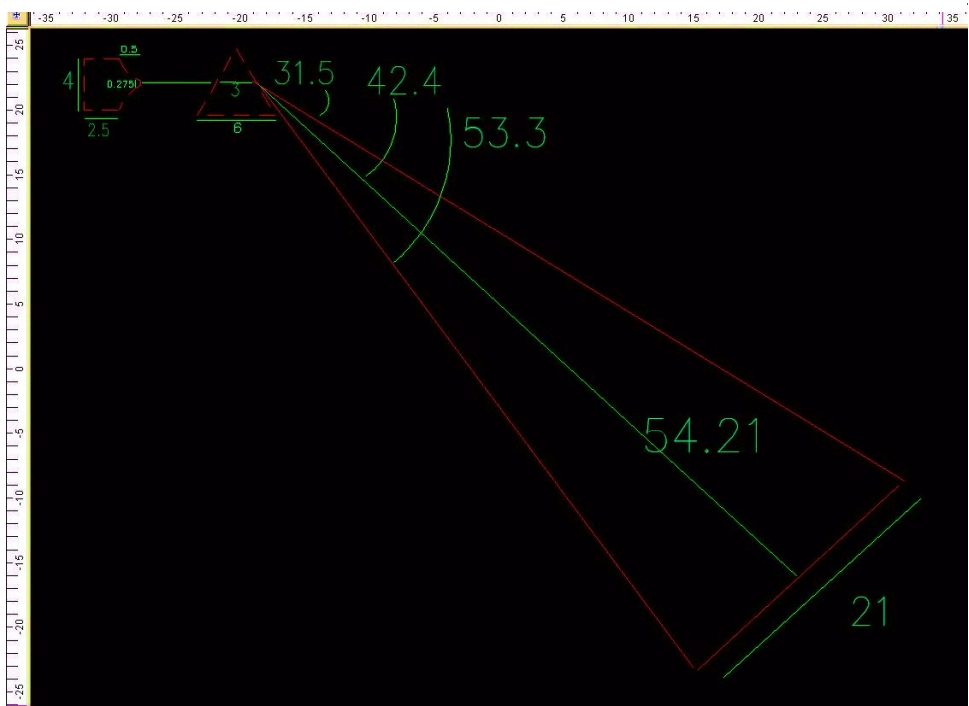
This imaging technique Modern FIB machines can easily achieve a resolution of 5 nanometres (further imagine resolutions may lead to undesired milling of the specimen). During the milling process, the whole system has to be under a vacuum so that air molecules do not disrupt the beam of ions. This is another limitation of using electron microscopes and FIB. It means that living organisms cannot be imaged and so some life processes of cells cannot be viewed to a high resolution.

2.6 The dimensions of the structure are designed on CAD (Computer Aided Design) software and the file can be uploaded to the FIB (Focused Ion Beam) machine. Using this software, I was able to

produce different designs for the optical elements I would use. The software allowed me to precisely design and determine the dimensions of the prism and jetting structure so that an accurate design of the structures could be milled. I produced many different designs on the software and consulted with specialists to determine which jetting structure would produce the best beam. I chose one from 8 different designs for the jetting structure. I also produced a diagram of how the experiment would be set up, including the correct angles of refraction and the distance from the screen to the prism, which helped to determine the feasibility of the setup of the experiment.



Jetting structure CAD designs



CAD of the setup of the experiment

The software used by the

machine converts the design into a pattern, which it mills onto the silicon. I uploaded different designs and set different doses of current for the milling process and measured the depth to which the structure was milled. This allowed us to determine the relationship between the dose and the milling depth. For example, a current of around 0.3 nano amps would mill a depth of around 2 microns. From this relationship between current and depth, I determined the settings for the FIB that would produce the structures with the most desirable properties. After milling the structures, I etched them using hydrofluoric acid. Hydrofluoric (HF) etching is a widely used process, which uses a strong acid to cut into the unprotected parts of the sample. This was so that the milled structures would have greater definitions around the edges so that the optical elements would be formed with a greater quality. The silicon sample was left in hydrofluoric acid for approximately half an hour. After neutralising the HF acid and drying, I then coated the silicon in a layer of PDMS.

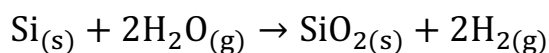
2.7 PDMS is an organic silicon based polymer, widely known for its unusual flow properties. It is a silicon oxide chain with two methyl groups bonded to each silicon atom. Intermolecular forces attract the chains to each other, which keeps them together unless an external force, which is stronger than the intermolecular forces, is applied. Strong hydrogen bonds form between the oxygen and hydrogen atoms. The partially positively charged hydrogen atoms are attracted to the lone pair of electrons on the oxygen atom, which is a region of negative charge. This attraction holds the chains close to one another. Hydrogen bonds are the strongest type of intermolecular bonds and that is why the PDMS elastomer has a very high viscosity. Upon mixing the PDMS elastomer with the curing agent (hardener), it turns from a viscous liquid to a rubbery solid. The curing agent increases the number of cross-links between the polymer chains, thus decreasing the ease of which the polymer chains can slide over each other and therefore hardening it. Due to the increase in number of crosslinks, a stronger externally applied force is needed to separate the chains and so they hold together and form a solid. The elastomer and curing agent are added in a 10:1 ratio. The number of crosslinks will increase as more curing agent is added. To prevent the mixture from becoming too hard or too soft, the precise ratio has to be added. Also, if the curing agent is not thoroughly mixed with the elastomer, then it will lead to some regions of the mixture becoming unusually hard and other regions very soft. As the elastomer is too viscous for the curing agent to properly diffuse, it must be stirred. After stirring, the mixture is placed in a vacuum oven. The vacuum will cause the air bubbles in the PDMS to rise to the top and be removed. Air bubbles within the PDMS could severely affect the light beam travelling through it by causing it to refract in random directions before emerging from the prism. It is therefore important to ensure that all the air bubbles are removed from the PDMS. I therefore leave the sample in the vacuum for a long time (2 to 3 hours) so I can be certain that there are no air bubbles and reduce the limitations or risk to the validity of the experiment. PDMS is commonly used as surfactants, which lower the surface tension between two liquids or a liquid and a solid and also as anti-foaming agents. However, it has been found that they also have excellent optical properties, approaching that of glass. Due to this and the ease of which I can manipulate the polymer into different shapes and structures, I have chosen it to be the material used in our experiment. Multiple samples of the milled structures were produced to test and determine the best layering techniques for PDMS, e.g. the thickness of the PDMS layer.

The silicon sample would act as a mould for the PDMS. The PDMS would cover the silicon sample and fill the spaces where the optical elements were milled. The PDMS with the silicon sample would then be heated in a vacuum oven to solidify the PDMS. Heat would cause curing agent to diffuse within the mixture and would also allow the cross links to form. The layer can then be peeled off so that you obtain the fully formed microstructures made out of PDMS.

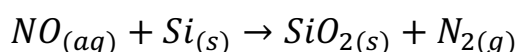
2.8 A problem I encountered when trying to remove the PDMS layer from the silicon was that the adhesion was stronger than expected. This meant that when I tried to peel off the PDMS layer, it would lose its integrity and split into smaller pits, which were still adhered to the silicon. To try and solve this problem I formed a thicker PDMS layer on the silicon sample so that it would hold its

integrity. However, this did not work because the PDMS was still strongly bonded to the silicon so the region around the milled structures would not peel off and instead it would break away from the thick PDMS layer when I tried to remove it. I placed the sample in a plasma asher that would use an oxygen plasma to try and remove the rest of the PDMS from the silicon sample so that it could be reused. Plasma ashing is a process, which removes light-sensitive material from an etched wafer. The plasma source generates reactive atoms (for example oxygen or fluorine), which combine with the material to form an ash. Gas at low pressure is exposed to high power electromagnetic waves (radio waves), which ionise the gas atoms. The electromagnetic waves increase the energy of the atomic electrons and cause them to increase to an energy level, which the atom cannot accommodate and so the electron is removed from the atom, leaving a positively charged ion. This process is carried out under vacuum so that the ions do not react with any other molecules and a plasma is formed. I used high temperature plasma ashing to try and remove as much PDMS as possible. At lower temperatures the plasma would only remove residual material. The ash, formed from the reaction between the PDMS and the plasma, is then removed by a vacuum pump.

However, I found that not enough of the PDMS was removed from the silicon, which meant that I had to mill completely new structures. If I were to use the same sample and try and remove the PDMS, by scraping it off for example, I would risk damaging the optical elements in the process, which would affect the behaviour of light whilst passing through and in between the structures. It was speculated that the PDMS would adhere less strongly if an oxide layer of around 100nm was grown on the silicon. To grow the oxide layer, the silicon sample was placed in a tube furnace under wet oxidation (reacted with steam). Each oxygen atom in the water molecules form two covalent bonds with a silicon atom and in the process the two hydrogen atoms are displaced. The hydrogen ions bond to form hydrogen gas. Silicon can form four bonds, which means that two oxygen atoms can bond with it (since one oxygen atoms forms two covalent bonds with the silicon atom).



The formula above shows the reaction to form an oxide layer. The oxide layer also tinged the sample blue, which was expected. I used a thermal oxide calculator to determine how long the oxidation process would take for a specific temperature. I calculated a time of 44 minutes at a reasonable temperature of 900C. This temperature was used because it would significantly speed up the oxidation process without damaging the silicon or equipment. Increasing the temperature would increase the rate of reaction so the oxide layer would form quicker. However, it would also be much more costly to maintain such high temperatures and the risk of accidents and damaging the substrate would also increase. I chose to increase the temperature to 900C because the oxide layer would form relatively quickly and the temperature can also be maintained safely and inexpensively. To further ensure that the PDMS would completely unbind from the silicon, I treated the sample with a mixture of hydrofluoric and nitric oxide. The nitric oxide would oxidise the silicon to silicon oxide and the hydrofluoric acid would etch away the silicon oxide to leave the PDMS sample. The formula below shows the oxidation of silicon using nitric oxide.



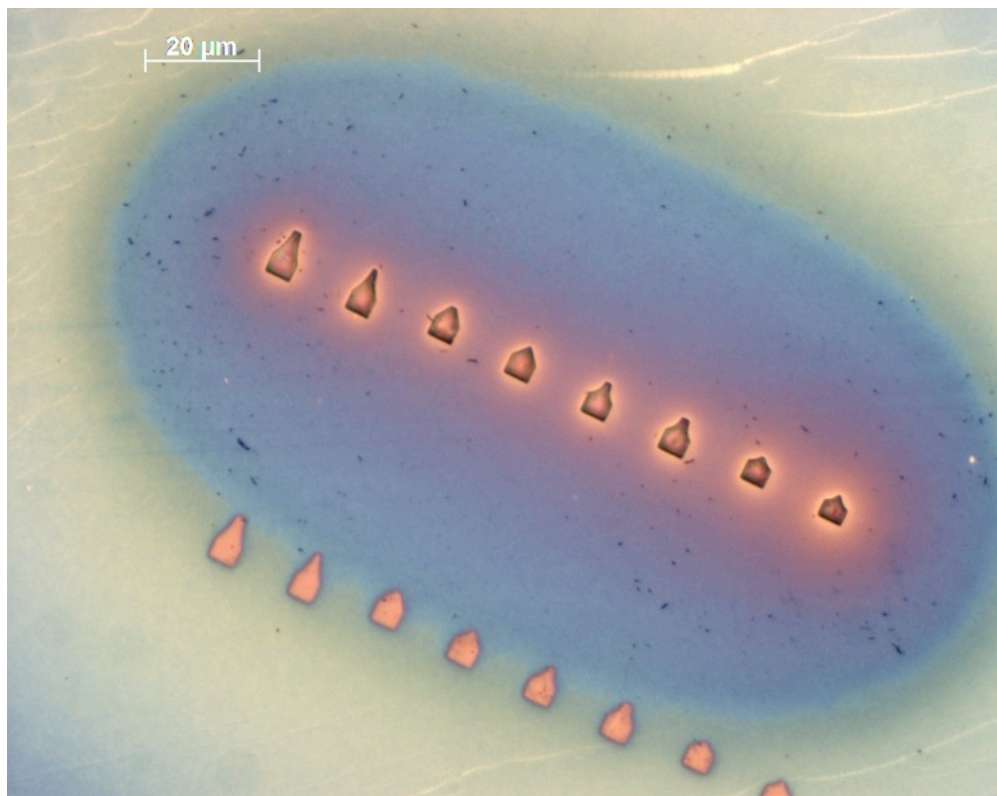
There is also the possibility that the nitric acid could oxidise the PDMS, since it is silicon based, and cause some deterioration. However, the deterioration of the PDMS would be low compared to the silicon sample. This is because it is easier to break the bonds within silicon than it is to break the bonds within PDMS. After etching overnight, I was able to remove the silicon from the PDMS sample without damaging it. The sample was then viewed under an optical microscope to ensure that the

structures were fully formed and not damaged. Defects in the optical elements would otherwise disrupt the light ray through the jetting structure and the prism. If I happened to find visible defects with the structures, I would have repeat the procedure and mill new structures or I could use the same sample if all the PDMS could be successfully removed. To produce the spectrum, I would shine light through the jetting structure to produce a beam incident to the prism. The prism would then refract the beam and separate the white light into different wavelengths (colours). A blank screen would be set up with the prism being in between the jetting structure and the screen. It would also be tilted at the correct angle so that a full clear spectrum could be viewed. Increasing the length between the prism and the screen would result in the spectrum appearing more blurred and decreasing the length would be lead to the different wavelengths merging so that there would no longer be a clear contrast between the different colours.

3. Results and discussion

Due to defects of the PDMS structures, I was unable to produce a beam. The jetting structure was not produced of sufficient quality to allow a beam to form, which was most likely due to the techniques that were used to remove the PDMS from the silicon. The structures may have become distorted or some parts may have stayed bonded to the silicon. This would mean that it would not have been fully formed and so it could not effectively produce a beam of light. In addition, peeling off the layer of PDMS from the silicon would mean breaking the bonds between the silicon and the PDMS optical elements. Although these bonds are weaker than the bonds between the PDMS molecules they are still relatively strong. To break the bonds I stretched them until the weakened and broke away from the silicon. However, when stretching the bonds to weaken them the bonds between the PDMS would also have inevitably been stretched and cross-links between the polymer chains would have been broken. If enough cross-links were broken, then the polymer chains would only be weakly bonded to each other and the material would not be able to regain its original form and remain permanently distorted. If more cross-links are broken, then the elastic limit of the PDMS would be much lower and it would undergo plastic deformation (permanent distortion) more easily. Therefore, the material would have different densities in different regions and this may affect the refractive index, since the refractive index increases with an increase in optical density. Since there would be a range of refractive indexes within the PDMS, light may refract multiple times and split up into its different components (wavelengths) before emerging from the prism so that there was no observable pattern. Light may have also refracted many times inside the jetting structure and split into different wavelengths so that an intense beam could not be produced and therefore there would be no beam of light to enter the prism. Another reason why the refraction pattern was not observed may be due to the light was directed at the system. I planned to use an optical fibre, however I reached the conclusion that this would not work as it would have been extremely difficult to properly align the fibre with the base of the jetting structure and also to shine light through the other end of the fibre. I therefore decided to shine light directly at the jetting structure using an ordinary torch, as it would be able to collect the light and form a much more intense beam than the torch, which the prism could refract. This was a much quicker and easier procedure than trying to use an optical fibre, however a disadvantage was that if the light forming the refraction pattern was not intense enough, the light from the torch could have been intense enough to mask the refraction pattern. There would have been a greater chance of observing the diffraction pattern if I had managed to concentrate the light into the jetting structure so that no light from the source would be able to reach the screen and the light forming the refraction pattern would be of the greatest intensity. Furthermore, the nitric oxide acid may have oxidised a more significant amount of PDMS so that more of the structure was etched away by the hydrofluoric acid than intended. Extensive etching of the PDMS using the mixture of nitric acid and hydrofluoric acid may have also lead to defects in the jetting structure and prism. Rough handling of the PDMS and silicon could also have affected the quality of the structures. For example,

scratching of the silicon surface or distortion of the PDMS due to stretching or extreme temperature change when trying to unbind the PDMS from the silicon. The oxide layer that I grew may have also been too thin, which meant that it would have a negligible effect on the adhesion between the PDMS and silicon.



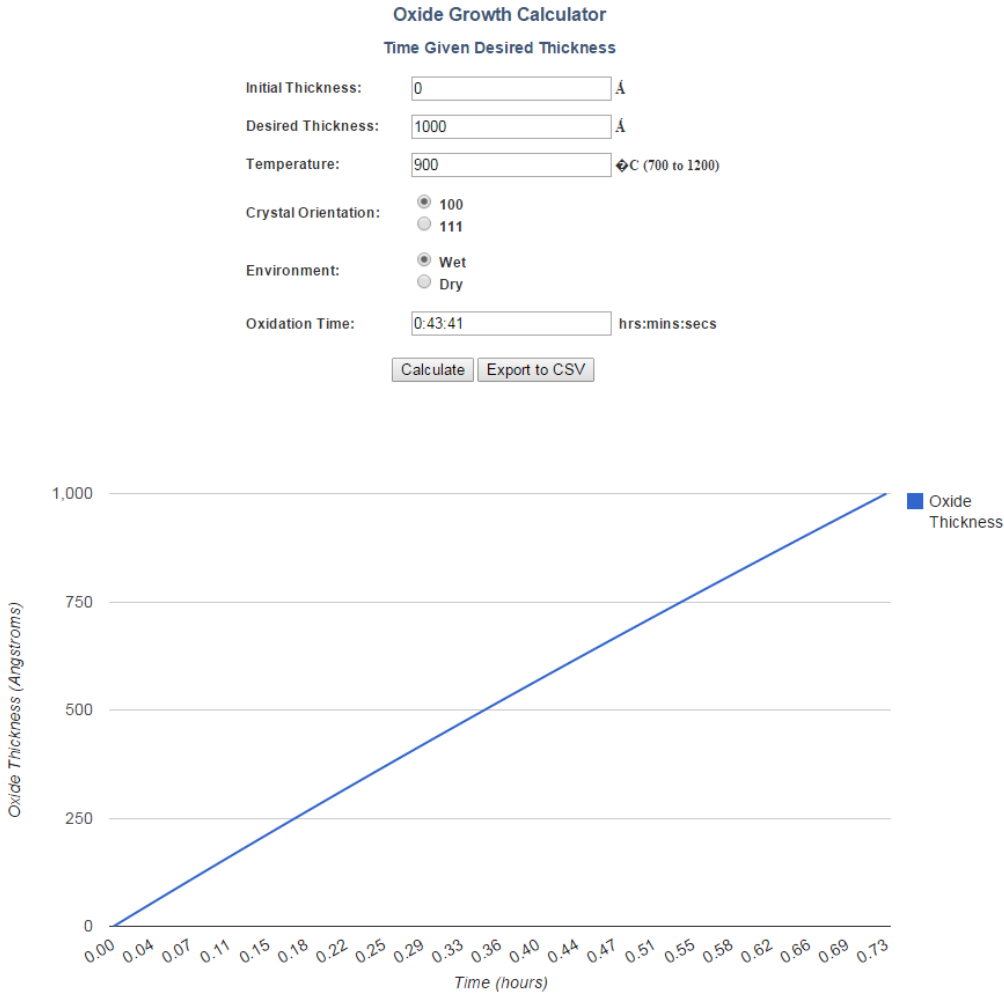
Milled jetting structures

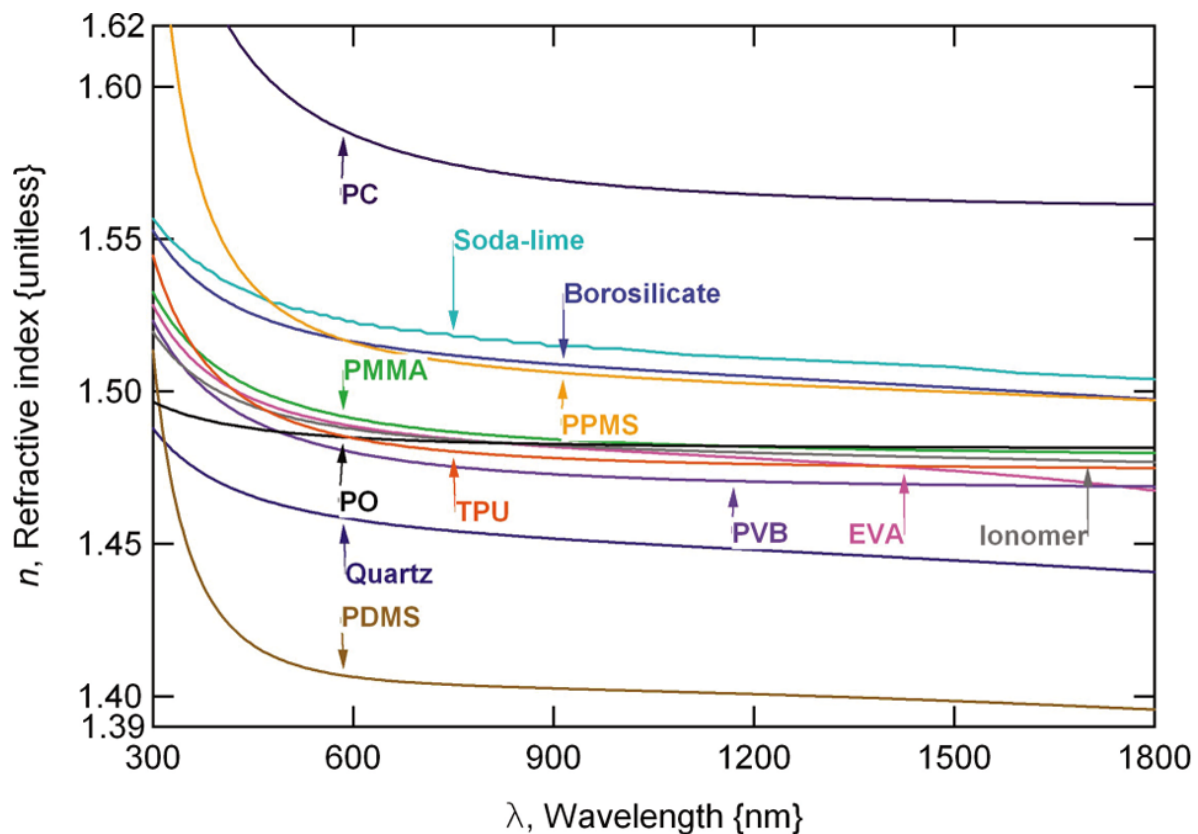
4. Conclusion

The next step in our experiment would be to treat the silicon surface with a coating that would prevent the PDMS from binding as strongly to the silicon and make it easier to peel off. I would use either a nickel or chrome coating, as the adhesion between these materials to PDMS is weaker compared to PDMS and silicon. This would mean that I would be able to remove the PDMS from the silicon without damaging the microstructures. As the bonds between the PDMS and chrome/nickel would be weaker, when peeling off the PDMS there would be less chance of breaking as many cross links between the PDMS polymer chains so therefore it would be able to regain its original shape after being distorted. The quality of the micro optical elements would therefore be maintained. Adding a coating would also help to clean the surface of the sample so that there would be less or no impurities left. Removing impurities would decrease the possibility of them interfering with the light beam or the refraction pattern. Another option would be to mill the structures in a different substrate, such as glass. This would adhere less strongly to the PDMS so that it could be removed more easily. It would therefore also not require a coating and the cross links between the polymer chains in the PDMS would remain intact. However, because I would no longer be using silicon and instead a completely different material with different properties (such as hardness), I would have to recalculate the dose of current needed to mill the structures to particular depths using FIB. I could also try growing a thicker oxide layer and ensure that the whole sample surface would be oxidised by leaving it in the tube furnace for a longer period of time. A known solution to removing PDMS is by immersing the whole

sample in a quaternary ammonium fluoride such as TBAF (Tetrabutylammonium Fluoride) and a non-hydroxylic aprotic solvent such as PMA (propylene glycol methyl ether acetate). This technique has been found to remove PDMS at a rate of 1.5 microns per minute, which is approximately five times faster than traditional dry etching methods. However, I was unable to use this technique due to the danger of handling TBAF, which is extremely toxic, corrosive and carcinogenic. Although I did not achieve my ultimate goal of observing the behaviour of light near the diffraction limit, I did obtain significant data and research from carrying out the manufacture and processing of the optical elements, which in turn can help me determine specific conditions and requirements for conducting similar experiments. Such investigations and experiments may include milling different structures using FIB for specific processes and functions or researching the interaction between certain substances.

5. Appendix





6. References

Thermal oxide calculator -

<http://www.cleanroom.byu.edu/OxideTimeCalc.phtml>

Removing PDMS from silicon –

<http://www.sciencedirect.com/science/article/pii/S0167931715002488>

Refractive index of PDMS-

<http://opticalengineering.spiedigitallibrary.org/article.aspx?articleid=1157700>

Diffraction limit -

https://en.wikipedia.org/wiki/Diffraction-limited_system

Silicon wafer processing -

http://www.cleanroom.byu.edu/EW_formation.phtml

[https://en.wikipedia.org/wiki/Wafer_\(electronics\)](https://en.wikipedia.org/wiki/Wafer_(electronics))

PDMS -

<http://www.fao.org/ag/agn/jecfa-additives/specs/Monograph1/Additive-315.pdf>

<http://www.rsc.org/chemistryworld/2015/07/polydimethylsiloxane-pdms-silly-putty-podcast>

FIB -

http://www.nanolab.ucla.edu/pdf/MRS_Bulletin_2007_FIB_machining.pdf

http://www.nonmet.mat.ethz.ch/Infrastructure/FIB/FIB-SEM_Introduction_JR.pdf