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Fabrication of Large Mechanically Flexible Multi-Layered PDMS Optical Devices

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A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science

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Abstract

Mechanically flexible large area polydimethylsiloxane (PDMS) optical devices are fabricated using soft-lithography techniques based on replica moulding. These non-rigid optical devices can be designed as sheets to act as either light concentrators (collectors) or diffusers (illuminators) based on the position and geometry of micro-optical structures (MOSs) embedded within the sheet or imprinted on its surface. The active surface area of the device can range from less than a sq. cm to several sq. m. The performance of the large area optical device is a function of the location and geometry of micro-optical structures, thickness and shape of the flexible waveguide, core and cladding material (ie. refractive indices), and the wavelength of the incident light source. A centrifugal casting technique that simultaneously de-gasses and fills a patterned, thin mould cavity is introduced as the backbone to the proposed fabrication methodology. Combined with the ability to control the refractive index of PDMS and a partial curing technique that bonds subsequent layers, a bottom-up layer-by-layer fabrication process is proposed and described in detail.

Keywords: Flexible large area optical device, soft lithography, polydimethylsiloxane (PDMS), polymethylmethacrylate (PMMA), micro-machining, micro-optical features, centrifugal casting, partial curing
To The Reader: A Digital Age

Hello and thank you for your interest in my M.E.Sc project and thesis! I have added several PDF features in an effort to utilize our digital age and make this thesis as easy as possible for you to follow/extract information from. The following is a list of these added digital features with a brief explanation on how they work:

- **General Hyperlinking:** The table of contents and each figure, table and equation reference in the text has been hyperlinked in red to its corresponding element. Clicking one of these red reference links will jump you to its location in the document.

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- **Abbreviations & Nomenclature:** Instances that appear in paragraph text have a small hover tool-tip added to them. If you’ve forgotten what a symbol or abbreviation means while reading, simply hover over it with your mouse to see its long-form. Try it: PDMS.

**Note:** Hover tool-tips may only work on higher-level PDF readers, such as Adobe Acrobat Reader. Other readers may implement this feature at a later date.
Acknowledgements

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List of Terminology, Abbreviations and Nomenclature

Terminology

centrifugal force

For ease of understanding, the term *centrifugal force* is described as the reaction force to the centripetal force in this research. Centrifugal force is considered a fictitious force, also called a pseudo force, whose motion can only be described using a rotating frame of reference.

collector

An optical device which takes a large area of incident light and concentrates it to a specific internal region for harvesting.

illuminator

An optical device which takes a relatively small, but intense light source and diffuses it out from a large area surface.

Abbreviations

- CAD: computer-aided design.
- CCD: charge-coupled device.
- CLTE: coefficient of linear thermal expansion.
- CNC: computerized numerical control.
- CPU: central processing unit.
- DUVI: deep ultraviolet irradiation.
- IR: infrared.
- LCD: liquid crystal display.
- LED: light emitting diode.
- MOS: micro-optical structure.
- PDMS: polydimethylsiloxane.
- PETG: polyethylene terephthalate glycol-modified.
PMMA  poly(methyl methacrylate).
QED    quantum electrodynamics.
TIR    total internal reflection.
TiO$_2$ titanium dioxide.
UV     ultraviolet.

**Nomenclature**

$E_{\text{energy}}$  Energy.
$E$                Elastic modulus.
$\varepsilon$      Permeability.
$\varepsilon_r$    Dielectric constant.
$\eta$             Index of refraction.
$\lambda$          Wavelength.
$\mu$              Permittivity.
$\theta_{\text{crit}}$ Critical angle.
$c$                Speed of Light.
$f$                Frequency.
$h$                Planck’s constant.
$v$                Phase velocity.
eV                 Electron volts.
Chapter 1

Introduction

1.1 The Problem

Control and manipulation of propagating light waves is an emerging area of technology that will significantly impact a variety of fields such as solar energy collection, visual communication, medical, and the entertainment industry. This waveguiding technology can act as either light concentrators (collectors) or light diffusers (illuminators) based on the position and geometry of micro-optical structures (MOSs) embedded within the device. Some early commercial successes where propagating light waves are controlled in this manner are often found in the solar industry or for electronic displays. A common attribute of these optical devices is they are designed and fabricated using rigid materials and thus do not flex or bend. Current solar collectors [1–4] and light guide plates for electronic displays [5–10] are fabricated with hard plastic or glass. Flexibility is a desirable quality for these types of devices since they can potentially be fabricated as an optical waveguide sheet which can conform to any under-lying surface.

Major problems associated with designing flexible optical devices are the optical materials available and the fabrication process to create them. Research on small-area flexible illuminators [11–14] and collectors [15] do exist for display back-lights and solar harvesting, respectively. These designs have been fabricated in a lab environment so the process is quite tedious and slow while also having similar application issues equivalent to current rigid designs. Current flexible illuminators and collectors are designed to utilize the low refractive index of air \( (n_{\text{air}} = 1) \) for total internal reflection (TIR) to occur within the core of the waveguide. This design approach limits the potential of these devices to applications which are not subject to the elements or much wear. Take the back-lights in electronic displays for example, the illuminator is always encased so the MOSs will never become damaged. Alternatively, in solar collectors the MOSs that concentrate light rays are often relatively large, making them durable,
however small air-based MOSs for re-directing light towards solar cells are underneath the rigid waveguide; thus they are again protected. It would be desirable to have MOSs internal to a waveguide, such as between core and cladding layers making them inherently protected. The challenge then becomes finding material(s) with multiple refractive indices and an efficient fabrication methodology to create these internal MOSs within a flexible optical device.

1.2 Applications of Large Area Flexible Optical Devices

It is first and foremost essential to define what a truly large area waveguide is. In research, a palm-sized optical device can be considered to have a very large area. For example, Guo et al. [16] developed a 5 mm$^2$ metallic photonic crystal and defined their research as having a large area. In this case the definition of large area is likely relative to the size of the MOSs present in the device. For instance, if nano-scale structures are present, there may be millions of structures within a 10 cm$^2$ area, therefore in relative terms these waveguides are often considered to have a large area. In regards to this research, the size definition of an optical device or sheet is not relative to the size or number of MOSs present. In fact, the MOSs for these flexible devices can be of any size as long as they are sufficient towards the proposed functional design goal. Thus, the definition of large area in this research is simply anything of sufficient size for the practical application at hand which can range from a few cm$^2$ to several m$^2$. This definition of large area is one of the most important considerations when developing the scalable fabrication methodology detailed in this research.

Adding flexibility to the design of optical devices, such as large area sheets, opens up many new potential applications. These applications for deformable polymer optics include any uses upon changing non-planar surfaces such as: flexible luminescent sheets for wearable displays [17], low-level light phototherapy [18, 19] and a cloth based pulse oximeter [20]. Additionally, in a general and imaginative sense, collectors and illuminators may now be fixed onto variable surfaces. For example, a runner’s jacket with a flexible collector on the surface could act as a solar concentrator to harvest sunlight and supply power to electronic devices or even an internal air conditioning unit to keep the runner cool. The suit could also use an illuminator to light up in the dark of night instead of the traditional reflective approach used today. The point is, key applications for flexible illuminators and collectors are for surfaces which change and vary with use. Otherwise, a rigid device designed for a specific non-planar surface would likely be far more efficient.


1.3 Research Motivation

Current flexible optics mainly exist in communications. These flexible optics are designed to transmit optical data from point A to point B in optical interconnects [21–25]. These are designed as thin planar waveguides so they can package well within small electronic devices for a future where optical data transfer surpasses the present electrical data transfer between components. The materials used are often rigid, but are thin enough or stacked in a certain way [23] to be capable of bending to low radii with minimal data loss. These interconnects are not of a truly flexible variety and would not be able to conform onto variable non-planar surfaces whereas a truly flexible material would. Truly flexible optical materials exist that are capable of conforming to any underlying surface. One such flexible optical material is polydimethylsiloxane (PDMS) which has a very low young’s modulus that varies from 360–870 kPa [26] rendering it as a truly flexible and elastic material. PDMS has certain properties (discussed in section 2.6.2) which are ideal for soft-lithography, replicating complex micro/nano structures and transmitting visible light. Unfortunately, due to relatively long cure times, temperature dependant shrinkage, and trapped gasses in the viscous pre-polymer PDMS has been a difficult material to use in fabrication, especially on an industrial scale. Therefore, not only would it be desirable to create truly flexible illuminators and collectors, but having an efficient and scalable fabrication process with potential for other optical devices in industry would be a great contribution to science and technology.

1.4 Objectives of Research

The primary objective of this research is to develop an entirely new and scalable fabrication methodology for creating robust flexible optical sheets that may act as illuminators, collectors or a combination of the two. The keywords here are scalable and robust. When these two keywords are applied to the fabrication methodology it means that the techniques used should not be limited to a laboratory environment and instead be capable of creating both small and large area optical devices for a multitude of applications. When only the fabricated product is considered, a robust version is one that can withstand wear, the elements and unforeseen potential applications. An example of a flexible illuminator that would not be considered robust is the flexible liquid crystal display (LCD) back-light developed by Lee et al. [11] where the MOSs are present on the diffusing surface of the device. These MOSs would become damaged in any application where this featured surface is subjected to wear. Therefore, this is not a robust design since it can only be used in applications where the MOSs are always protected by an encasing. A robust version of this illuminator would be able to protect itself and thus
could be used for this application as well as many others.

Other objectives of this research are to reduce the overall fabrication time and complexity while maintaining functionality and quality in flexible optical devices. In current literature, these types of products have been limited to the lab environment. Therefore, time consuming and complex fabrication methods with expensive lab equipment are common in this area of research to maintain quality and function. For the prospect of more efficient and simpler fabrication, an industry-level approach to the overall methodology is considered.

1.5 Overview of the Thesis

This thesis is organized into five Chapters. Chapter 2 provides a detailed overview of light’s propagation properties and its potential limitations in regards to the design of flexible optical devices. The goal of Chapter 2 is to introduce the reader to light at both the small photon scale and the larger optics scale to define constraints and supply insight towards the choice of flexible waveguide materials. After sufficient light-related insight is achieved, the Chapter will explain how multi-layered flexible optical devices function and the vast considerations that must be present when developing a scalable fabrication methodology. Chapter 2 will conclude by identifying PDMS as the ideal candidate for flexible transparent materials and thoroughly reviewing PDMS-based fabrication techniques found in literature to acknowledge that a combination of these fabrication techniques will be required.

Chapter 3 describes the proposed combination of fabrication techniques used to create a working and scalable methodology. The methodology uses a novel centrifugal casting technique to simultaneously degas, inject, and fill the MOSs within a thin mould cavity. A PDMS partial curing technique alongside a careful peel of an elastomeric master pattern is also utilized to build multiple layers in a bottom-up fashion. By patterning the top surface of each layer with MOSs through soft-lithography, each new partially cured surface essentially becomes a new master pattern; thus internal MOSs can be fabricated. Being a proof of concept research project, the potential limitations of the proposed methodology are also addressed.

Chapter 4 details the experiments and resultant prototypes to prove the feasibility of the proposed fabrication methodology in Chapter 3. Fabrication of a combined collector-illuminator prototype as well as a 3-layer illuminator design is detailed and discussed. First, an overview of the fabrication equipment used is detailed where additional technical information can be found in Appendix C. Afterwards, the prototypes are illuminated and imaged to display their functionality and show the existence of multiple layers where internal MOSs exist within the illuminators. Both prototypes are fabricated in a cost-effective manner using the proposed method and prove the overall feasibility of the methodology that has been developed.
Finally, conclusions are presented in Chapter 5 with many recommendations for future work. Since there exists several important, yet unrelated aspects encompassing the proposed fabrication methodology there is plenty of room for future work towards optimizing the design and process.
Chapter 2

Literature Review of Large Area Flexible Optical Devices

2.1 Introduction

The first demonstrated attempt at controlling light occurred by accident in 1841 by Swiss physicist Jean-Daniel Colladon [27]. He was showing the flow of water through various holes of a tank in an attempt to see the breaking up of water jets. The lecture hall audience complained they were unable to see the water jets so Colladon directed sunlight into his tank hoping to illuminate them. He noticed the light followed the curved stream from his tank until the jets broke apart. What he had just discovered is the phenomenon known as total internal reflection (TIR) which was the key stepping stone towards today’s modern optics and is detailed in Section 2.2.4 below.

Now, fibre optics are one of the most familiar and common forms of waveguiding technology in modern optics and communication [28]. They transmit light from one point to another using TIR, similar to the way light had travelled through Colladon’s curved stream of water. A device that transfers light from one location to another is considered to be one of the simplest forms of optical devices which is known as a simple waveguide. Photonic crystals, on the other hand, are one of the most complex forms of optical devices [29, 30]. These crystals have certain micro and nano optical structures within them that individually act as a separate waveguide, however these waveguide paths are so small that they only allow certain wavelengths (or colours) of light to pass. An opal gemstone is an example of a naturally occurring photonic crystal. In this research the optical devices are not designed to filter certain wavelengths of light, but are still more complex than simple waveguides. They are designed as flexible planar sheets which act as either diffusers (illuminators) or concentrators (collectors), but they
ultimately use the same core principles to function. Figure 2.1 illustrates examples of these functional optical devices. An illuminator takes a concentrated source of light, such as an illuminated edge, and diffuses it to escape the largest surface of the device to essentially act as an illuminating sheet. A collector does the opposite, it takes incident light from the largest surface of the device and concentrates it to a specific location within, such as an edge; it essentially works as a light harvester. When the prospect of adding flexibility to the working principle of these planar diffusing and concentrating optical devices is considered, an entirely new realm of design and fabrication complexity is introduced.

![Figure 2.1: Illustration of a simple diffusing/illuminating optical device (left) and a simple concentrating/collecting optical device (right).](image)

This Chapter presents a literature review of the working principles, design considerations and potential fabrication techniques for flexible illuminators and collectors. Being a fabrication-oriented thesis, a thorough explanation of the basic and atomic properties of light is presented in Section 2.2 to define key design constraints. Then, Sections 2.3 and 2.4 describe the working principles of waveguides with the differences between illuminators and collectors. Sections 2.5 to 2.6 supply insight towards a robust monolithic design and how to achieve it. Finally, Section 2.7 reviews several techniques used in the literature for fabricating polydimethylsiloxane (PDMS)-based devices which eventually compiles into the proposed fabrication methodology presented in Chapter 3.

### 2.2 Properties of Light

Light is a subset of electromagnetic radiation and travels in (observable) oscillations or waves with a constant wavelength. The term *observable* is within parenthesis because light at the quantum scale can be described as both waves and particles. In 1929 Albert Einstein presented to the world that light is made up of particles and that the flow of light is a wave [31]. This is a very complex topic within the field of quantum electrodynamics (QED) which is beyond the scope of this research. However, it is important to realize some of the concepts at smaller scales to better understand how light travels through different media. Therefore, this section will briefly explain some of light’s strange interactions with matter at these scales to supply insight
towards potential optical device design constraints and material selection. In this research the term *light* will refer to the portion of the electromagnetic spectrum covered by the field of optics which consists of visible, ultraviolet (UV) and infrared (IR) (Figure 2.2). In optics, light is treated as rays; all propagating light in this research is described with arrows and lines to depict light rays (i.e. Figure 2.1).

![Optics Region](image)

**Figure 2.2:** Optics region of the electromagnetic spectrum. (Modified from [32])

### 2.2.1 How Light is Created

Light and all electromagnetic radiation consists entirely of the elementary particle known as photons. A photon has zero mass and charge, thus it does not steadily lose energy over time and will always travel at the universal precise speed limit of 299 792 458 m/s in a vacuum, also known as the *speed of light*, $c$ [33]. Photons are created when electrons transition from high to low energy states within an atom. The energy of a photon is inversely proportional to the wave-
length it (observably) travels at which is given by the photon energy equation (Eq. 2.1) \cite{34} where \( E_{energy} \) is energy, \( h \) is Planck’s constant with a value of \( 6.63 \times 10^{-34} \) J\( \cdot \)s, \( c \) is the speed of light, and \( \lambda \) is the wavelength.

\[
E_{energy} = \frac{hc}{\lambda} \tag{2.1}
\]

Additionally, since frequency, \( f \), is related to wavelength using Eq. 2.2, Eq. 2.1 may also be simplified into Eq. 2.3.

\[
f = \frac{c}{\lambda} \tag{2.2}
\]

\[
E_{energy} = hf \tag{2.3}
\]

When enough energy is added to an object, for example a slab of iron, the human eye will begin to see the emitted photons as the colour red (620 – 750 nm) as they begin to reach energy levels within the visible spectrum.

### 2.2.2 Absorption, Reflection & Transmission

All materials exhibit some degree of absorption, reflection and transmission of light and each occurs from a single interaction: an electron absorbs a photon \cite{34}. The absorption of photons occurs in an exact opposite manner to which they were created. There is emphasis on the term exact because for an electron to absorb a photon the energy level of the photon must precisely match the original high-to-low energy state transition which created it. Any photons that do not match these required energy levels are simply ignored by the electron and essentially pass through the medium without any interaction with matter. After absorbing a photon the electron is then in an excited state and is thus unstable. This electron now has two options: transfer that energy elsewhere or re-emit an equivalent photon. If the absorbed energy is equal to one of the electron’s natural frequencies of vibration (Eq. 2.3) then resonance will occur which increases those vibrations further causing interactions with neighbouring atoms and ultimately converting the absorbed photon into thermal energy. An electron’s natural frequencies are dependent upon the molecule(s) and crystalline structure it composes. If the energy absorbed does not match an electron’s natural frequency then the electron, being in an unstable excited state, will fall back to a lower energy state to re-emit an equivalent photon to be later absorbed by subsequent electrons. The re-emitted photons are now considered either reflected or transmitted where the interface between two separate media dictates whether the photon is sent back within the same medium (reflection) or sent into the new medium (transmission). Figure 2.3 depicts a simple illustration of many photons interacting with a new medium. A portion of the photons are absorbed, reflected and transmitted upon the medium where the amount of each is dependent on the new medium’s material properties. The angles which light is reflected at
are dependent upon an object’s surface roughness and the atomic structure which makes up the object. There are two main types of reflection: diffuse and specular (which can also apply to refraction). Diffuse reflection is when light gets reflected at many angles. Light will reflect in many angles off a rough surface, but will also transmit into the irregularities of a surface to reflect multiple times within the molecular structure before escaping back in the general direction to which it entered. Specular reflection is when light gets reflected at the same angle and is capable of forming images. A very smooth surface, such as a mirror, will create images using specular reflection as the light is sent back at its incident angle. This is due to a tightly packed molecular structure with many free electrons that will not allow light to enter. Conductors, such as many metals, have tightly packed molecules in a lattice structure with free electrons, thus light is mostly reflected via specular reflection when these conductors have polished surfaces. Glossy paints or polished non-conducting surfaces are examples where both diffuse and specular reflection occur.

**Figure 2.3:** How light interacts with a new medium to become absorbed, reflected and transmitted.

The term *transmittance* is used to describe the fraction of propagating light which transmits through a medium. Alternatively, the term *attenuation* is used to describe how much light is lost through a medium and can be defined as either a fraction or in decibels per unit length. The transmitted intensity of light through a medium will depend upon the amount of incident light that was reflected upon entering the medium and the amount of light absorbed through the medium. Since the absorption of light occurs from the specific energy levels of electrons in atoms, it is important to consider the wavelengths of light which will be used in a device’s application when selecting a material. For example, glass would be a poor choice of waveguide material for an application involving UV light (10 – 380 nm) as it absorbs these wavelengths [35]. This means that glass’s crystalline structure and molecules share natural frequencies with the energy levels of UV light so these photons are completely absorbed and
2.2.3 Light Propagation

When a material appears completely transparent it is due to no free electrons blocking the incoming light and electrons not having many natural frequencies which coincide with the visible spectrum of light. Additionally, there must be no gaps or holes in the material’s molecular structure which causes the scattering of light. Water and snow, both consisting of $H_2O$ molecules, are great examples where light scattering effects transparency. The $H_2O$ molecules have very few natural frequencies which absorb visible light. However, since snow has many gaps of air or gases within it while water has none, one appears transparent while the other does not; the lack of transparency is due to the scattering of light.

In a transparent material with no gaps or holes, visible photons are continuously being absorbed and re-emitted throughout the medium. This absorption and re-emission of photons from atom to atom in any medium is known as light propagation and is how light travels through different media. As previously mentioned, the speed of light in a vacuum, $c$, is equal to 299 792 458 m/s. However, when light travels through a medium filled with atoms, such as visible photons through a solid transparent medium, the light appears to be slowed. There are two theories that contribute to the change in apparent speed of light in different media. The first theory is the photon absorption-emission theory which describes a small delay between the absorption and re-emission of photons from atom to atom, but the light is still travelling at $c$ in a vacuum between each interaction [34]. The second theory is the interference theory which attempts to explain the observable phase velocity direction change of light entering a new medium while its frequency remains constant. The interference theory can be understood from Maxwell’s equations for electromagnetic waves in a vacuum [36] (See Appendix A.3).

To understand the macroscopic propagation of light, it is important to realize how a photon actually travels. When a photon moves from point A to point B it will simultaneously take every possible path to reach its destination where the actual path it takes can only be explained using QED. This is known as Fermat’s principle [37] (see Appendix A.4) and for simplicity’s sake, the basic understanding required is that a photon travelling from point A to point B will always attempt to choose the path that takes the least amount of time: a straight line. Thus, in this research light is depicted as rays. Figure 2.1 in Section 2.1 and Figure 2.3 above illustrate examples using straight rays to describe light. It is only necessary to consider light as waves and particles when photons interact with new media of matter whose geometric dimensions are close to or smaller than the wavelengths of propagating light; this information is extracted into micro-optical structure (MOS) geometric constraints in Section 2.2.5.
2.2.4 The Law of Refraction and Total Internal Reflection

When light enters a new medium at any angle other than 0° from the normal it is not only transmitted with a change of speed, but it also undergoes a change of direction. The change in direction is due to the change in phase velocity, \( v \), which is the speed the crests of a wave moves at while its frequency remains constant. This phenomena of light changing velocity upon entering new media is known as \textit{refraction} and is one of the key properties for manipulating light at the macroscopic scale. All lenses in commercial optical devices function using refraction. Refraction is described by Snell’s law which can be derived with Fermat’s principle of least time [37]. Snell’s law states that for two differing media and a wave with a single frequency, the ratio of the sines of the angle of incidence \( \theta_1 \) and angle of refraction \( \theta_2 \) is equivalent to the ratio of phase velocities between the two media [38]. Snell’s law is given by:

\[
\frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{v_1}{v_2} \tag{2.4}
\]

Snell’s law can also be described in terms of the materials’ index of refraction, \( \eta \), which is a dimensionless number that describes how light propagates through a medium at an apparent slower velocity and is given by:

\[
\eta = \frac{c}{v} \tag{2.5}
\]

where \( c \) is the speed of light in a vacuum and \( v \) is the phase velocity of light in the medium. After substituting Eq. 2.5 into Eq. 2.4, Snell’s law becomes:

\[
\frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{\eta_2}{\eta_1} \tag{2.6}
\]

Figure 2.4 illustrates this phenomena of refraction by using a ray of light travelling from point A to point B in the least amount of time. Since the phase velocity of light is lower in the second medium (\( v_2 < v_1 \)) the angle of refraction \( \theta_2 \) is less than the angle of incidence \( \theta_1 \).

Light’s incident angle upon a new medium will dictate how much of the light is reflected or refracted by the new medium. Fresnel equations (see Appendix A Section A.1) can be used to describe the complex behaviour of light between media of differing \( \eta \) [39]. There are a few special cases with Fresnel equations which depend on a light ray’s angle of incidence. Light polarization, the single plane oscillation of light waves, is a familiar special case for refracted light that occurs at a specific angle between media known as Brewster’s angle (see Appendix A Section A.2) [40] and is how polarizing sunglasses work. Another special case which is most important to this research occurs when light propagates from a high \( \eta \) medium to a low \( \eta \) medium at a large angle with respect to the normal. Between these media there exists what
is known as a critical angle, $\theta_{\text{crit}}$, where any incident light at or greater than this angle will be completely reflected back into the higher $\eta$ medium. This phenomenon is known as total internal reflection (TIR) and is another key property for controlling and manipulating the flow of light [41]. TIR is how all waveguides work to transmit light from one end to the other and occurs when Snell’s law (Eq. 2.6) becomes impossible to satisfy where $\sin(\theta_2)$ must be greater than one. Figure 2.5 illustrates TIR once this critical angle is reached. The critical angle, $\theta_{\text{crit}}$, can be found by rearranging Snell’s law when $\theta_2 = 90^\circ$ or $\sin(\theta_2) = 1$. $\theta_{\text{crit}}$ is then given by:

$$\theta_{\text{crit}} = \arcsin \left( \frac{\eta_2}{\eta_1} \right)$$

(2.7)

Using the law of refraction and TIR it is possible to control how much light escapes or
stays trapped within a medium of higher $\eta$ compared to surrounding media. For illuminators and collectors small geometrical structures, termed MOSs with lower $\eta$ can be embedded within the medium to accurately control how much light escapes or stays trapped at certain regions. For example, in illuminators MOSs such as wedges can be used to modify the angle of a portion of the total propagating light rays so that $\theta_1$ becomes less than $\theta_{crit}$ and this light will now escape the higher $\eta$ medium upon interaction with the next interface. The function of these MOSs and their geometrical shapes are detailed in Section 2.4.3.

2.2.5 Limitations of Light as Optical Device Design Constraints

A working knowledge of light and how it propagates through a material allows for some design constraints and insight for illuminators and collectors. The following three constraints and material selection insight have been arbitrarily defined from the working knowledge described above.

**Constraint: Micro-optical Structure Size**

The first constraint considers the interference theory of light mentioned in Section 2.2.3. Thomas Young performed an experiment in 1801 using two small slits with dimensions close to the wavelength of visible light [42]. When light passed through these slits Young observed an interference pattern on the screen. This interference pattern was caused by a phenomenon called diffraction where light sightly bends as it passes around the edge of an object [43]. The amount of bending depends on the relative size of the wavelength of light to the size of the opening. Therefore, in relation to the design of illuminators and collectors it is important to set a size limit on the diffusing and concentrating MOSs. MOSs that are too small within the nanometre scale will cause interference and scattering of the propagating light waves which is difficult to control due to the randomness of light scattering at that scale. This will impede upon the intended affect to uniformly illuminate or collect light if the application requires it. Therefore this first arbitrary constraint sets a minimum feature dimension size of $0.005 \text{ mm}$ or $5 \mu\text{m}$ which is five times larger than low-level IR light.

**Constraint: Layer Thickness**

The second constraint relates to the thickness of the medium in which light will propagate through the flexible illuminators/collector. Once a medium with propagating light due to TIR becomes thinner than the wavelength of light, it may interfere with itself and simply ignore a boundary change and escape. For example, when the thickness of a medium is a quarter-multiple of the wavelength of propagating light, the TIR waves from both surfaces interfere to
cancel each other out. When the thickness is a half-multiple of the wavelength, both reflections interfere and add to each other. For visible light this increase and decrease of intensity of certain wavelengths will be observed as certain colours escaping the medium. This natural phenomenon is called thin-film interference and is what causes the unique multiple colours of a soap bubble [44]. Additionally, once this medium’s thinness approaches the size of wavelengths it may interfere with what is called an evanescent wave. A side effect of TIR described in Section 2.2.4 is where an evanescent wave appears beyond the interface of media. Essentially, even though the entire incident light wave is reflected back into the higher $\eta$ medium, there is some penetration into the lower $\eta$ medium at the boundary. Thus, when the higher $\eta$ medium becomes thin towards the wavelengths of propagating light it can interfere with this evanescent wave and the transmittance will decrease. Therefore, the multiple layers of illuminators and collectors should not be too thin to affect the larger wavelengths in the optics region (Figure 2.2). Thus, an arbitrary constraint can be made to design the layers of these optical devices at a minimum thickness no thinner than a sheet of paper (0.05 mm). The term thin in this research will revolve around this scale where layers can be as thin as 0.05 mm or as thick as 5 mm depending on the intended application.

**Constraint: Refractive Index Consistency**

The third constraint is simply to keep the refractive index, $\eta$, constant throughout each layer within the optical device. If $\eta$ varies through a medium the light can be bent or focused. Additionally, since transmittance and refraction are relative to the wavelength of light a change in $\eta$ may begin to absorb certain wavelengths. This type of material is known as a gradient-index medium which can be very difficult to control and fabricate. Gradient-index mediums are seen in the human eye where the $\eta$ of the lens varies from approximately 1.406 in the central layers down to 1.386 in less dense layers of the lens [45]. Therefore, if attempting to modify the $\eta$ of a layer, this change in $\eta$ should stay constant throughout the layer to avoid any unintended changes in the propagating light’s direction and transmission. Alternatively, if the $\eta$ can be precisely controlled new potential design options may open for controlling the flow of light; however, this is beyond the scope of this research.

**Insight: Flexible Transparent Material Selection**

Insight towards creating or modifying flexible materials that transmit light within the optics spectrum is valuable information. This may be potentially useful in future work (Section 5.3) considerations for synthesizing new flexible polymers or modifying the refractive index, $\eta$, of current materials. For creating new transparent materials, Section 2.2.2 described the absorp-
tation, reflection and transmission of photons in different media which were dependent upon the electron configuration and crystalline structure within the media. When optical transparency is a desirable aspect for a material, there are several properties at the molecular scale involved, however two key properties define most solid transparent materials. The first key property was mentioned in Section 2.2.3 which described a consistent crystalline structure with no gaps or holes was essential to prevent the scattering of propagating light. The second key property is a solid material’s band gap which is the energy range where no electron natural frequencies can exist [34]. The band gap is typically described in electron volts (eV), a unit of energy equal to $1.6 \times 10^{-19}$ J. Using Eq. 2.1 and converting to eV, visible light is within the range of approximately 1.8 eV to 3.1 eV meaning if a material’s band gap is greater than 3.1 eV it will be transparent due to no natural frequencies available to resonate. Thus, when an electron is excited past the band gap it simply falls back down and re-emits an equivalent photon as described in Section 2.2.2. Insulators often\(^1\) have band gaps which are greater than the range of visible light and do not have a “sea of electrons” (found in conductors) to reflect and block light from entering in the first place. For modifying the refractive index of existing transparent materials the dielectric constant is closely related. To show this, the phase velocity in a medium is inversely proportional to the permittivity, $\mu$, and the permeability, $\epsilon$ of the material and is given by [34]:

$$v = \frac{1}{\sqrt{\epsilon\mu}} \quad (2.8)$$

Substituting Eq. 2.8 into Eq. 2.5 gives:

$$\eta = \frac{c}{v} = \frac{\sqrt{\epsilon\mu}}{\sqrt{\epsilon_0\mu_0}} = \sqrt{\epsilon_r\mu_r} \quad (2.9)$$

where $\epsilon_r$ and $\mu_r$ are the relative permittivity and the relative magnetic permeability, respectively. Finally, since most materials are only slightly magnetic ($\mu_r \approx 1$) Eq. 2.9 simply becomes:

$$\eta \approx \sqrt{\epsilon_r} \quad (2.10)$$

Relative permittivity, $\epsilon_r$, is also known as the dielectric constant. Therefore, a transparent material’s $\epsilon_r$ is directly proportional to its refractive index, $\eta$. This is particularly useful when searching for initial candidates or for tuning a material’s $\eta$ by adding high $\epsilon_r$ particles to the material’s matrix. Section 2.6.3 describes adding high $\epsilon_r$ nano-particles to the chosen material

\(^1\) It is possible for a conducting material to be transparent if it has a large enough band gap and a “sea of electrons” with natural frequencies outside the wavelength range of visible light. Indium tin oxide is an example of such a conductor and has a band gap of approximately 4 eV; this material is often used in many touch-screen electronic devices due to these unique properties of being right on the edge of conducting and transparency.
in this research for tuning its $\eta$.

**Conclusion**

Table 2.1 below presents a summary of the arbitrary constraints and insight described above. This information can be used as a guideline for the design and transparent material selection for illuminators and collectors as well as any other potential optical device.

Table 2.1: Initial design constraints/insight for flexible diffuser and concentrator applications.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Constraint/Insight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feature size</td>
<td>$&gt; 5 , \mu m$ to avoid light scattering and interference</td>
</tr>
<tr>
<td>Propagating layer thickness</td>
<td>$&gt; 0.05 , m$ to avoid interference effects</td>
</tr>
<tr>
<td>Propagating layer material</td>
<td>Must have constant $\eta$ to avoid unintentional bending, focusing, and absorption of light</td>
</tr>
<tr>
<td>Transparency</td>
<td>Related to band gap and insulators</td>
</tr>
<tr>
<td>Refractive index ($\eta$)</td>
<td>Related to the dielectric constant ($\varepsilon_r$) for modifying $\eta$</td>
</tr>
</tbody>
</table>

**2.3 Operating Principles of Flexible Optical Devices**

Optical devices such as fibre optics or simple waveguides used in communications utilize the phenomenon of TIR described in Section 2.2.4 to function. Fibre optics exist as two transparent materials with different indices of refraction, $\eta$. Figure 2.6 illustrates the flow of light in a simple fibre optic cable’s cross-section using rays. The light propagates through the core ($\eta_1$) and is totally internally reflected by the cladding ($\eta_2$). Therefore the $\eta$ of the core must be higher than the $\eta$ of the cladding ($\eta_1 > \eta_2$) for TIR to occur. The core and cladding in fibre optic cables are cylindrical and are designed to transmit light in the form of data from one end to the other. The core and cladding typically consists of different transparent hard plastics or glass materials. These cables are flexible to a certain degree since the diameters of both the core and cladding are very small. The ability to be considered flexible with rigid materials due to small diameters can be understood from the classic bending stress in a beam equation [46]:

$$\sigma = -\frac{M_y y}{I_x}$$

(2.11)
where $\sigma$ is the bending stress, $M_x$ is the moment about the neutral axis, $y$ is the perpendicular distance to the neutral axis, and $I_x$ is the second moment of inertia about the neutral $x$-axis. Looking at the second moment of inertia for a cylinder’s cross-section shows that it is proportional to the quartic of the diameter:

$$I_{x,\text{circle}} = \frac{\pi D^4}{64} \quad (2.12)$$

Therefore, since $D$ is in the numerator in Eq. 2.12 and $I_x$ is in the denominator in Eq. 2.11 the stress due to bending in a cylinder decreases rapidly as the diameter shrinks. This applies for all geometrical shapes and is why thin objects such as sheet metal are easily bent. However, like all hard materials with a high elastic modulus, $E$, there is a limit to bending before plastic deformation or breaking occurs. Practical usage of fibre optic cables typically does not require a high degree of bending during usage. If sharp bending is a requirement, there exists right-angled mirrored Sections to direct light around tight corners.

![Figure 2.6: Illustration of light rays propagating through a fibre optic cable’s cross-section. Light propagates through the Core and reflects off the Cladding from TIR. There is often a Jacket for protection.](image)

### 2.3.1 Structure of an Optical Sheet Device

Optical sheets function in a similar manner to fibre optic cables. In fact, the cross-sectional illustration in Figure 2.6 above properly depicts the cross-section of a simple waveguiding sheet having a jacket and how it functions with the same behaviour. Instead of a core and a single cladding enveloping it, a sheet must consist of a set of layers in a cladding-core-cladding fashion for TIR to occur. An optical sheet, or in this example a strip, is often more desirable than cylindrical cables in optical interconnects [21–25] due to the ability to have multiple channels of differing information running along the strip as well as the overall packaging ability a thin strip has compared to multiple cables.
2.3.2 Bending Losses

All optical devices functioning with TIR will be subject to bending losses. When light propagates through the core medium of a simple waveguide it is internally reflected at many angles and does not follow a precise ray path as explained in Section 2.2.3. Therefore, when bending occurs some angles of propagating light will change and become lower than the critical angle, \( \theta_{\text{crit}} \), between the core’s \( \eta \) and the cladding’s \( \eta \) (Eq. 2.7). When the incident angle between the core and cladding mediums becomes lower than \( \theta_{\text{crit}} \) the propagating light will no longer totally internally reflect back into the core medium. The light that is not internally reflected will then escape into the cladding and eventually into the next medium (air). Light propagates at many angles, thus not all light will escape simultaneously upon initial bending. Instead, an increasing amount of light will escape as the bending radius decreases causing more of the light’s incident angles to become lower than \( \theta_{\text{crit}} \) in the bending region. As Eq. 2.7 depicts, a greater \( \Delta \eta \) between the core and cladding mediums will allow for a larger \( \theta_{\text{crit}} \); thus, less propagating light will escape during bending. Reducing bending losses in optical communication is a large area of study where achieving smaller bending radii with minimal attenuation loss is desirable, especially in optical interconnects [21–25].

2.4 Characteristics of Optical Light Concentrators (Collectors) and Diffusers (Illuminators)

Illuminators and collectors are not designed for light transmission from point A to point B. Instead, these sheets may comprise of multiple layers consisting of many MOSs which redirect light within the medium. Such large area waveguiding designs may act as diffusing sheets (illuminators) or light concentrating sheets (collectors). Rigid collectors [1–4] are typically designed for solar energy collection to concentrate light towards a smaller region where efficient solar cells convert the light to electricity in a cost-effective manner. Rigid illuminators [5–10] are often designed as diffusing panels for electronic displays known as light guide plates. Both collectors and illuminators utilize TIR with MOSs to control the incoming or outgoing light. These devices have many potential applications as they can manipulate light in a uniform or non-uniform fashion depending on the location and geometry of MOSs embedded in the device. This section will briefly describe the key parameters these devices function upon as well as how to optimize and evaluate different designs.
2.4.1 Source Lighting

Collectors and illuminators function in a similar, yet opposite manner. Figure 2.1 in Section 2.1 depicts a simple illustration of this similarity. The source lighting for a collector is always outside the device and lands upon its largest functional surface where it collects, redirects and essentially concentrates the light to an edge(s) or point(s) within the core medium. Source lighting for many existing collectors [1–4] is typically the sun as these are designed for solar energy collection. An illuminator takes an intense light source, such as an illuminated edge, and redirects, reflects and essentially diffuses the light out of the largest functional surface. These light sources are often fixed to the edge of the device [5–10] for propagation through the core medium. It is important to note that in both illuminators and collectors the incident and diffused light never propagate entirely in the exact same direction. Since light flows as a wave and reflects off many objects in the environment there are many incident angles of light upon collectors. Similarly, in illuminators the initial edge-lit source will propagate light at many different angles which will undergo TIR multiple times until escaping from diffusing MOSs. The diffused light in illuminators will also propagate out of the functional surface at many different angles. Therefore, it is important to have a robust design capable of functioning with as many different angles of incoming and outgoing light as possible. Alternatively, if a single polarization of light is desired, Brewster’s angle described in Section 2.2.4 could be used to achieve such an affect and is ultimately up to the designer to achieve it.

2.4.2 Selection of Core and Cladding Material

For a simple waveguide to function properly using TIR, the core and cladding must have differing material properties in order to have a $\Delta \eta$ between the two. Section 2.2.5 described how the dielectric constant is closely related to the $\eta$ of transparent materials. Since the $\eta$ of the core material must be higher than the $\eta$ of the cladding material for TIR to occur, Eq. 2.10 shows that the core material must also have a higher dielectric constant than the cladding. This can be used for the initial material selections, however there are more properties to consider than only the $\eta$. A key property to consider is the compatibility in bonding between the two materials. If the two materials cannot naturally adhere to each other then creating a layered cladding-core-cladding structure will become increasingly difficult. Using compounds such as an intermediate adhesive layer between the two materials for bonding is not a worthy solution as the thin adhesive layer will have its own $\eta$ and will essentially end up acting as the cladding layer instead of the intended material. Therefore, the two materials must bond without any intermediate help from other materials. If the two chosen materials do not naturally adhere, there exists techniques such as corona treatment [47], also known as air plasma treatment, which can
increase the surface energies and allow for bonding. These techniques may slightly alter the molecular properties of each surface, thereby also potentially changing the intended $\Delta \eta$ at the interface, which must also be considered in material selection.

Another key property to consider is the mechanical flexibility of the bonded materials. Mechanical flexibility is measured by the maximum possible deformation without permanent damage and is determined by the material’s stiffness which encompasses the yield strengths and geometries of the device’s materials. Equations 2.11 and 2.12 in Section 2.3 showed that as the diameter of a beam decreases, the stress due to bending rapidly decreases, allowing for more deformation before permanent damage. This is similar for the thickness of an object, such as a sheet, and relates to the geometric portion of stiffness and flexibility. The other portion depends greatly on the elastic modulus of the material. Both can be understood from the classic axial stiffness equation:

$$k = \frac{AE}{L} \quad (2.13)$$

where $k$ is stiffness, $A$ is the cross-sectional area, $E$ is the elastic modulus, and $L$ is length. Since both $A$ and $E$ are both in the numerator, the stiffness of an object will decrease as the thickness and modulus decreases. These properties ultimately specify the strain exerted within the deformed device. Elastic materials, such as rubber, perform exceedingly well in this regard since they have a low elastic modulus and return to their original shape and size when the forces which deformed them are removed. In general, materials with $E < 5$ MPa are often very elastic (i.e. natural rubber has an $E$ of $1$–$5$ MPa [48]).

Assuming the materials are capable of naturally bonding, if their stiffness differ by a large margin then during deformation there can be concentrations of stresses at important regions within the optical device, such as the plane where MOSs for diffusing or concentrating light exist. This can potentially permanently damage these MOSs and compromise the functionality of the device. Hu et al. [23] explains this challenge in waveguide and photonic design when using different thin stiff materials. They describe a “neutral plane” where the strain during deformation vanishes and how to determine or specify its location by stacking multiple thin materials. By forcing the neutral plane to exist within the optically featured core layer, Hu et al. [23] were able to achieve a minimum bending radii of $< 0.5$ mm despite the poor mechanical strength of the glass materials used.

In conclusion, several properties must be considered when selecting the core and cladding materials of flexible optical devices. Other considerations could even involve slow chemical reactions between the two materials that alter the $\eta$ over time. Therefore, the two materials must be considered together for compatibility issues and not separately solely for their $\eta$ and transparency. An ideal material selection for a truly flexible optical device is actually to use the
same base material in both the core and cladding layers. Using the same base material better ensures compatibility between layers for bonding and bending stresses. This is known as a monolithic design and is discussed in Section 2.5.3 below.

### 2.4.3 Importance of Micro-optical Structures

To manipulate and control the flow of light through an optical device, micro-optical structures (MOSs) must be present to reflect and refract the propagating light rays as desired. MOSs require very smooth surfaces to prevent the apparent randomness created due to the diffuse reflection and refraction of light that was discussed in Section 2.2.2. TIR or a metallic mirrored finish allows for reflection to occur off MOSs while refraction will occur if the $\theta_{crit}$ is not reached (Eq. 2.7) or the light is traversing from a lower $\eta$ medium to a higher $\eta$ medium such as a focusing lens. Both cases require the MOSs to have a different $\eta$ or reflective properties than the medium which the light is propagating within. The geometry, size, $\eta$, and locations of MOSs determine their function. Figure 2.7 illustrates three common MOS geometries: Pyramid/Cone, Convex Lens, and Wedge. These MOS geometries are commonly used in illuminators and collectors. For example, in illuminators with an edge light source wedges can be used to redirect propagating light rays to change their next incident angle upon the cladding to be less than the critical angle, $\theta_{crit}$; thus, light rays escape the device. Illuminators can utilize many different types of geometries to function since the propagating light often only needs a small change in angle to escape the core medium. MOSs such as holes, cones, dots, and even scores can redirect the light to a new angle which allows it to escape the device. For example, Huang et al. [5] and Park et al. [6] use micro-sized dots to diffuse light out of their designs.

![Figure 2.7: Cross-sectional illustrations of common micro-optical structures (MOSs). a) Pyramid or Cone for redirecting incident light into the core layer in many planar directions. b) Convex Lens for focusing incident light to a focal point below. c) Wedge for redirecting incident light in a general direction; i.e. to escape the core layer.](image)

Different geometries of MOSs can also be combined to create unique effects. Figure 2.8 illustrates the cross-section of a combination of a convex lens MOS and a pyramid MOS that...
can be used for light collection. The convex lens has a higher $\eta$ than the outside air ($\eta_1 > \eta_{air}$) and therefore the incident light is refracted and focused. This light then refracts more as it enters the core medium ($\eta_2$) and eventually the light hits the pyramid structure (with $\eta_1$) below. If the incident angle normal to the pyramid faces is greater than $\theta_{crit}$ between $\eta_2$ and $\eta_1$ then light will reflect off the pyramid due to TIR. This reflected light will have new propagation angles within the core medium ($\eta_2$) and if the angle is also greater than $\theta_{crit}$ between $\eta_2$ and $\eta_1$ it will reflect through the core medium due to TIR. Due to the geometry of a pyramid the incident light is now redirected to all four edges of the collector where sensors or photovoltaic cells may exist to harvest the light. Bouchard and Thibault [2] and Karp et al. [4] use similar light collecting techniques with their rigid collector designs.

![Figure 2.8: Cross-sectional illustrations of a MOS combination using a convex lens and a pyramid. The lens focuses incident light onto the pyramid which redirects the light throughout the core layer.](image)

The size of MOSs is also very important and, in general, smaller MOSs are often more desirable due to the ability to fit more within an area to create a more uniform distribution of incoming and outgoing light. The size of the pyramid relative to the lens and core thickness illustrated in Figure 2.8 is actually much too large for light collection to be efficient in a light collector with many of these MOS combinations. Light that is redirected off the pyramid will be propagating through the core medium and since the height of the pyramids are close to the thickness of the core layer ($\eta_2$) the rays have a high chance of striking adjacent pyramids. Therefore, in this example small and short pyramids relative to the lenses and core thickness, respectively are more efficient as there is less of a chance for redirected light to strike another pyramid on its route to the edges. Xie et al. [49] use prisms that are 1.8% the size of the lenses where the prisms have a base width of 90 $\mu$m and the lenses have a diameter of 5 mm to achieve an overall theoretical optical efficiency of 70%. This reduction in pyramid size relative to the lenses shows why the location of MOSs is also quite important. If the centre of the pyramid does not align with the centre of the lens’ focal point then light will not be evenly redirected.
to all four edges of the collector. Additionally, due to the micrometre scale MOSs are within, a slight alignment issue of a few micrometres can cause the focused light to miss the pyramids entirely. Therefore, accuracy of dimension, surface finish, material $\eta$, and alignment of MOSs is crucial in fabrication to ensure an efficient and functional product.

### 2.4.4 Importance of Core and Cladding Layer Thickness

A consistent and accurate thickness of the core and cladding layers is essential for a functional design. If a layer has a varying thickness then the angles of propagating light will slowly change and may unintentionally escape in certain regions of the core medium. If the thickness of a layer is not accurate it can cause unintentional interactions of light with MOSs and compromise the functionality or efficiency. Section 2.4.3 above described a MOS combination with a lens’ focal point hitting a small pyramid to redirect light. The thickness of layers also controls where the focal point of this lens will be upon the pyramid. Again, due to the micrometre scale of MOSs if the layer is thicker by even a few micrometres the focal point of the lens can miss the pyramid entirely. It is also important to mention that from Section 2.2.5 once the layers become very thin, approaching low multiples of the wavelength of light, issues with interference begin to occur. Therefore, a consistent and micrometre-accurate thickness of each layer must be achieved during fabrication for a functional and efficient product. Section 2.7.3 below details fabrication techniques used in literature to accurately control layer thickness.

### 2.4.5 Characteristics of Uniform and Non-uniform Illumination

Uniformity is an important property for many applications of illuminators and collectors and is controlled through design. For collectors the concentrated light is being directed to a specific location within the optical device, such as a point or edge where the uniformity of incident light at this location is far less important than the initial capturing uniformity. This is relatively simple to control with consistent repeating concentrating MOSs. A collector may require non-uniform initial light concentration in some applications and it is up to the designer to distribute the concentrating MOSs as required. For illuminators it is more complex and is highly dependent on the application and intended illumination effect. Consider a back-lighting application used in electronic displays where the source light is an intensely illuminated edge that is diffused out of the large surface facing the user.

In this application uniform illumination is of high concern to produce a bright even picture for the user. Figure 2.9 illustrates a simple non-uniform illuminator using diffusing wedge MOSs where the thickness of arrows represents the amount of light escaping in the general region. Since the wedge MOSs are all the same size and are distributed evenly through the
core layer a relatively large portion of the light is reflected and escapes upon hitting the first diffusing MOS. Less light hits subsequent MOSs until almost no light is available at the far end of the illuminator.

Figure 2.10 illustrates two common techniques to control uniformity: size and density of diffusing MOSs. Figure 2.10 on the left shows how the size of MOSs can control uniformity. MOSs closest to the source will have the most potential light to interact with. However, less light will interact with smaller MOSs allowing for a larger portion of the initial light to continue propagating towards subsequent MOSs. Figure 2.10 on the right shows how the spacing, also known as density, of same-size MOSs can control uniformity. Again, MOSs closest to the source have more light to interact with, but in this instance as the spacing between MOSs reduces the light interacts with more MOSs per unit length so as the intensity of light reduces the amount being reflected out also increases creating a uniform illumination. This density technique is generally easier to fabricate compared to the size technique due to the repeating geometries of MOSs. With controllable illumination, an example of an intentional non-uniform illuminator would be a sign where only the letters or image outlines are illuminated. The exact placement, density and size of diffusing MOSs will dictate where the main illumination occurs in this example. It is also important to note that smaller MOSs in illuminators will give a better resolution of light which will appear more uniform.
Many of the illuminators in the literature use these two techniques to control uniformity [5–9, 11, 12, 14]. Pan and Hu [50] even performed a theoretical and simulated study on how the density of simple diffusing MOSs affect uniform illumination and found that a reflective mirror located at the edge opposite to the source light helps efficiency. Other potential techniques may exist, such as gradient $\eta$ on MOSs or different reflective coatings throughout the core layer(s), however these techniques become increasingly complex to fabricate. In conclusion, uniformity is controllable in multiple ways which the designer can use to produce the intended illumination effect.

2.4.6 Estimating Performance and Light Loss

It is desirable to estimate the performance and efficiency of potential flexible illuminator or collector designs prior to fabrication. This is possible through ray tracing simulation on structured waveguiding models in multiple configurations. Zemax OpticStudio [51] is a ray tracing simulation software designed for optical engineers. Its main focus and capabilities revolve around sequential ray tracing of lens configurations for cameras and imaging, however it also has the capabilities of simulating complex lighting designs such as illuminators and collectors using non-sequential ray tracing. Nicholson-Smith [52] uses Zemax OpticStudio in her research to estimate the performance and overall efficiency of different illuminator and collector computer-aided design (CAD) which can be fabricated with this research. The illuminator parameters that are presented and fabricated in Chapter 4 are obtained from Nicholson-Smith’s [52] simulations and research. Figure 2.11 shows an example of the ray tracing capabilities and output in Zemax OpticStudio. The propagating light is treated as the simple rays that were described in Section 2.2.3. This design example uses the MOS combination that was illustrated in Figure 2.8 for concentrating and harvesting incident light. Figure 2.11 on the left shows OpticStudio’s ray tracing output of a single lens and pyramid MOS while the right image shows a collector design using these MOSs in a bent configuration of radius, $R$.

Efficiency of illuminators and collectors in bending is of high concern for flexible optics. Nicholson-Smith [52] was able to simulate and estimate the losses due to bending the small collector example shown in Figure 2.11 on the right. In general, the efficiency of a single structured layer in illuminator/collector design is a function of the probability that rays will strike MOSs while propagating through the medium. It is given by [52]:

$$\text{Efficiency} = (1 - D_p)^n$$  \hspace{1cm} (2.14)

Where $D_p$ is the density of MOSs, or pyramids in this example, and $n$ is the number of times the rays will strike the bottom face. Due to the complex geometry of this collector example,
efficiency equations such as this will become quite long. However, this is handled within the simulation software and Table 2.2 shows the overall efficiency due to bending this design at several radii. In this simulation the collecting surface with an array of lens MOSs has uniform incident light (i.e. not a point source of light) to show how much light escapes the layers solely from bending in an ideal scenario where all incident light is initially concentrated. Additionally, this example collector design is relatively small causing \( n \) in Eq. 2.14 to be low. As expected, the efficiency quickly decreases as the bending radius becomes smaller and propagating light rays begin to strike the medium interfaces at angles smaller than \( \theta_{\text{crit}} \), escaping the collector. In conclusion, estimations of a design’s performance and efficiency can be obtained through software such as Zemax’s OpticStudio allowing for design optimization prior to fabrication. Literature for rigid or flexible collectors and illuminators are often solely theoretical using simulation software such as OpticStudio [49, 53].

### 2.4.7 Measuring Performance and Light Loss

It is important to confirm if the simulations described in Section 2.4.6 above are accurate by evaluating and comparing illuminators and collectors fabricated with the same design parameters. With known \( \eta \) of layers there are multiple ways to measure efficiency and compare to simulations. One of the most simple and straight-forward approaches is to measure the light input and light output to obtain an approximate overall efficiency. Figure 2.12 illustrates a
Table 2.2: Zemax OpticStudio collector bend efficiency results

<table>
<thead>
<tr>
<th>Radius $R$ (mm)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>98.8</td>
</tr>
<tr>
<td>500</td>
<td>98.6</td>
</tr>
<tr>
<td>400</td>
<td>99.34</td>
</tr>
<tr>
<td>300</td>
<td>98.38</td>
</tr>
<tr>
<td>250</td>
<td>94.33</td>
</tr>
<tr>
<td>150</td>
<td>88.21</td>
</tr>
<tr>
<td>100</td>
<td>72.08</td>
</tr>
<tr>
<td>20</td>
<td>15.34</td>
</tr>
</tbody>
</table>

For comparisons to simulated data it is important for the experiment to have an identical set-up to the simulated one. This means that the detector should be at the same relative location and the curvature of the flexible optical device should match the curvature simulated. With modern technology this can be achieved by 3D-printing a fixture for taking measurements. By iteratively evaluating performance and comparing to simulations a potential calibration equation can be developed to better match simulated design with reality when designing for specific applications.
Figure 2.12: Illustration of a simple measuring system to compare light input to the output detected normal to the diffusing surface.

### 2.5 Design Considerations for Large Area Flexible Illuminators and Collectors

Designing complex large area optical devices is a difficult task. Luckily, modern simulation technology such as Zemax’s OpticStudio described in Section 2.4.6 is available to assess the performance or functionality of potential designs before fabricating. However, even with such advanced tools it is also important to consider the practical application, usage and manufacturability of potential designs. As mentioned in Section 1.2 large area is defined as a sheet with an area of a few cm$^2$ to several m$^2$ with MOSs of any size that fits the intended application. This opens up many potential applications for flexible sheets, but adds complexity in the fabrication of such large area devices. Therefore, illuminators and collectors should be designed for both practical usage and fabrication.

#### 2.5.1 Design for Robustness

The term *robust* can be defined as “strong and effective in all or most situations and conditions”. In relation to illuminators and collectors this means a robust design can be used for many different applications. As mentioned in Section 1.4 the flexible liquid crystal display (LCD) back-light developed by Lee et al. [11] cannot be considered very robust due to its limited encased applications. This is because the MOSs that allow the device to function as an illuminator are located on the outside surface which are thus vulnerable to wear and the elements in non-encased applications. A robust flexible illuminator design could not only be sold as a LCD back-light, but also for low-level light phototherapy where such a device will be handled multiple times. A way to achieve this in illuminator and collector design is for MOSs to be internal to the device. Figure 2.13 illustrates this concept where the MOSs are located...
between the core and bottom cladding layers. In this illustrative example the material which makes up the MOSs is the same as the cladding material because \( \eta_1 \) is already greater than \( \eta_2 \) for TIR to occur off MOSs. These internal MOSs are now protected by the cladding and will no longer become damaged from handling or the elements. This type of design strategy can be considered robust since it allows the device to function in many different applications without additional protection, such as the runner’s jacket described in Section 1.2. This design strategy for illuminators and collectors is not found in current flexible optical device literature due to the added complexity in fabrication. Internal MOSs creates new issues with the alignment and bonding of layers, however the fabrication methodology presented in Chapter 3 solves these issues through a combination of fabrication techniques which allow for a layer-by-layer building process.

![Figure 2.13: Illustration showing internal wedge MOSs penetrating into the core layer from the cladding layer creating a robust illuminator design.](image)

Another important robust design consideration is to design for the expected light loss during bending. In a simple waveguide a greater \( \Delta \eta \) between core and cladding layers will give a smaller \( \theta_{crit} \) and since incident light angles greater than \( \theta_{crit} \) will be subject to TIR this creates a larger range of angles to become internally reflected. When MOSs are concerned, the geometry and size also plays a major role in determining if TIR will occur. This geometry can be tuned for TIR to occur more during bending, such as in applications where a flexible optical device will be in a curved state more often than a horizontal state. Just before \( \theta_{crit} \) is reached and TIR occurs, most of the incident light is being internally reflected. Therefore, the geometry of MOSs can be tuned so there is 90% internal reflection off them in a horizontal state and 100% internal reflection in a more curved state which can help with uniformity in a number of applications. The size of MOSs will cause a similar effect. If the MOSs are larger then they will essentially bend and change geometry more over their reflecting surface when flexing the optical device compared to smaller MOSs which will not be altered in bending as much. This makes the MOSs follow the curvature to a larger extent where the \( \Delta \eta \) between layers becomes more important. In any case, it is important to design collectors and illuminators for their intended application, especially if the application requires smaller radii of bending compared to larger radii.
2.5.2 Design for Manufacturability

During the design stage, it is very important to know what type of fabrication technique(s) will be used. The illuminators and collectors in this research can range from a few \(cm^2\) to several \(m^2\) meaning that for MOS creation a large area patterning technique will be required. The patterning techniques used for creating internal MOSs will dictate the geometries which are possible. For example, if master patterns are created with traditional milling techniques, which do not have an area limitation, the tooling will limit the potential geometries. MOSs such as common pyramids or prisms used in most designs become increasingly difficult to fabricate with traditional milling due to tools leaving curved corners in negative pattern fabrication. On the other hand, photo-lithography is a very popular patterning technique that is capable of creating most geometrical shapes at both micro and nano scales, even the common pyramid or prism MOSs [4, 12]. Unfortunately, photo-lithography cannot pattern the large area requirement of these illuminators and collectors. Therefore, the MOS fabrication technique to be used must be known during the design stage to supply geometrical constraints. MOSs fabrication techniques on rigid substrates are detailed in Section 2.7.2.

Another important design consideration for manufacturability is the alignment of MOSs technique used. Section 2.7.4 briefly describes some alignment techniques used in literature. Ultimately, when any alignment technique is used, there will be an alignment tolerance. This alignment tolerance should be considered during the design stage to develop combinations of MOSs that still function properly at the worst-case maximum and minimum tolerances. For example, the lens and pyramid MOS combination that was illustrated in Figure 2.8 can be designed to have a similar functional alignment tolerance. The focal point created by the lens can be shifted downwards into the pyramid so that a larger area of light becomes incident upon the pyramid faces, allowing a minor misalignment to still direct light in all four planar directions to some degree. In conclusion, the techniques used for fabrication should be known during the design stage in order to create a design that is not only robust in application, but robust for fabrication as well.

2.5.3 Monolithic Design

Section 2.4.2 discussed the selection of core and cladding materials for flexible illuminator and collector design. It described how several aspects must be considered including material compatibility, stress and strain during bending, and the refractive index (\(\eta\)) requirements of both materials. A desirable design approach which avoids many of the bending and material compatibility issues is to use a single base material. Single base material design, or monolithic design, uses only one material throughout the design of an entire device. In regards to this
research, the core, cladding and MOSs would be designed and fabricated with the same material. Having the same material ensures compatibility between layers and allows for a better distribution of stress during bending due to very similar\textsuperscript{2} mechanical properties. For monolithic design to provide waveguiding capabilities, the core and cladding layers still require a $\Delta \eta$ for TIR to occur. Therefore, the monolithic material chosen must have the capability of having its $\eta$ modified. Section 2.6.3 discusses how to modify the $\eta$ of the chosen material for a monolithic design through doping, thermal and mixing techniques.

Even if using multiple materials and there are no compatibility issues nor prominent stress or strain issues during bending, it is still important to consider the effects of bending upon MOSs present in the device. In rigid designs, air is often used as the material medium for inner MOSs due to its low refractive index ($\eta_{\text{air}} \approx 1.0$) [2, 4]. When this concept is applied to flexible designs, there may be no apparent material issues, however the MOSs will deform during bending due to the large difference in material structure; solid vs. gas in this case. This deformation during bending can be solved to some degree by making the MOSs as small as possible. Ultimately, some deformation will still occur which affects how light will reflect off the structures. To avoid this, the medium for MOSs should consist of a flexible material with similar properties which a monolithic design approach solves and is used in this research.

### 2.6 Choosing a Flexible Optically Transparent Polymer for a Monolithic Design

To fabricate flexible optical devices it is essential to choose a truly flexible material. Unlike many current flexible designs which use very thin layers of polymers that could be considered rigid when slightly thicker [21–25], a truly flexible material is one that is capable of bending at a range of larger thicknesses. These types of materials are known as elastomers and have a low elastic modulus, $E$. Additional to flexibility, there are several other key material properties required related to the transmission of light which is discussed next.

#### 2.6.1 Required Key Material Properties

Section 2.2.3 described how light propagates through a material which creates a basis for the key properties required in transparent materials. Section 2.2.5 also described how the dielectric constant of insulators is related to the optical transparency of a material. This is particularly important when finding initial candidates or attempting to develop new transparent materials.

\textsuperscript{2}The term \textit{similar} is used due to the slight material composition changes caused by the $\eta$ modification required for monolithic design functionality which is detailed in Section 2.6.3
As a guideline, Table 2.3 lists key material properties for selecting a viable transparent material for flexible optical devices. The information is extracted from previous sections; it is arbitrary and based on experience with elastic materials and polymers.

Table 2.3: Key material property guideline for flexible multi-layer optical device material selection

<table>
<thead>
<tr>
<th>Property</th>
<th>Approx. Value or Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>High transmission of light</td>
<td>Visible and near IR must be &gt; 80%</td>
</tr>
<tr>
<td>High purity of material</td>
<td>No gaps or unintended impurities in material structure including potential gas bubbles created in fabrication</td>
</tr>
<tr>
<td>Low elastic modulus, $E$</td>
<td>$E &lt; 5$ MPa for elastic flexibility</td>
</tr>
<tr>
<td>Monolithic compatible</td>
<td>Must be able to modify the $\eta$ of the material and it must be possible for it to bond to itself</td>
</tr>
<tr>
<td>Cross-linking</td>
<td>Time to cure cannot have a long physical constraint (i.e. &gt; 10 hour cure). Must have the capability for reduction in cure times through optimization or other techniques</td>
</tr>
</tbody>
</table>

An additional desirable aspect of elastomeric material choice for this research is availability. Park et al. [54] synthesized their own flexible transparent polymers for optical interconnects. The process to synthesize their materials was lengthy and appeared complex to individuals without a chemical background. It would be inconvenient to continuously synthesize a material for fabrication experiments where obtaining a repeatable $\eta$ might become an additional challenge. Therefore, commercially available materials which align with the key properties in Table 2.3 above are ideal. One such material that meets all these requirements while also being commercially available is PDMS which is detailed in the next section.

2.6.2 Polydimethylsiloxane (PDMS)

Polydimethylsiloxane (PDMS) is a flexible silicone-based organic thermosetting polymer which is also optically transparent with a high transmittance ($> 95\%$) of visible and near infrared light [55]. It is available commercially from several suppliers where it consists of a base and agent to be mixed and cured thermally. PDMS is also inert, non-toxic, and non-flammable making it a very sought-after material for different applications in several fields of research. Other than elastic flexibility and transparency, PDMS has a very key attribute that makes it an invaluable material when considering its use for illuminators and collectors. The material has the ability to replicate almost any surface imperfections [56–58]. This soft-material replication
process is known as soft-lithography which is detailed later in Section 2.7.1. Soft-lithography capabilities are essential for creating MOSs within an elastomeric material since they can be fabricated on a variety of other materials and later replicated onto PDMS. Since MOSs can be fabricated on different materials, the number of fabrication techniques to create them is increased due to minimal material limitations. For example, since PDMS is an elastomer, it would very difficult to accurately remove material with traditional milling techniques. Instead, rigid materials can be MOS patterned with milling and then replicated onto PDMS via soft-lithography later.

PDMS is well documented because its viscoelastic, thermosetting and inert properties have made it the material of choice in microfluidics research [59–61]. PDMS is supplied in two-parts as a base and agent that require mixing and then a thermal cure to become a solid elastomer. This causes its mechanical and optical properties to vary with mixing ratio, temperature and cure time. Schneider et al. [62] compared the rheological, mechanical and optical properties of two different commercial PDMS products: Sylgard 184[63] and RTV 615[64]. They found that RTV 615 had better optical transmittance over a range of wavelengths (400 – 1750 nm) while Sylgard 184 had a slightly higher elastic modulus and faster cure times. Kim et al. [65] investigated the nonlinear mechanical properties of Sylgard 184 PDMS in relation to the mixing ratios of the base and agent. They found that the amount of curing agent used will change the elastic properties of PDMS where excess curing agent creates a hard PDMS and less curing agent creates a soft PDMS, both with differing stress-strain curves. Johnston et al. [66] investigated the mechanical properties of Sylgard 184 PDMS in relation to the curing temperatures from 25 °C to 200 °C. They observed a linear relationship between the elastic modulus, $E$, and the curing temperature, resulting in a doubling of $E$ from 1.32 MPa to 2.97 MPa over their range of curing temperatures. Liu et al. [67] investigated the mechanical properties of Sylgard 184 PDMS in relation to long cure times at high temperatures (100 – 500 ºC). They found that longer cure times at temperatures greater than 200 ºC largely reduces the mechanical strength of PDMS where the reduction is attributed to the thermal decomposition which starts at 200 ºC and reaches a peak at 310 ºC. Cai et al. [68] investigated the optical absorption loss in RTV 2 PDMS over a range of wavelengths (400 – 2500 nm) for multi-mode data communication. They found that losses in the 600 – 900 nm range were attributed to the CH$_3$-groups in the polymer which may be useful for tuning the polymer for specific wavelength ranges. They also verified that the optical properties of cured PDMS stay constant in high temperature environments. Having well documented information on a commercially available elastomer is very important. This means it is possible to estimate the mechanical properties of fabricated illuminators and collectors in relation to the mixing and curing conditions used in this research.

Unfortunately, PDMS has been considered difficult to fabricate complex devices with at
an industrial scale due to its relatively long cure times, temperature dependant shrinkage, and
trapped gasses in the viscous pre-polymer creating an interest in research related to industrial
fabrication approaches using the material [69, 70]. However, due to the ideal optical, flexibility
and replication properties of PDMS it has been the material of choice for the existing flexible
illuminators and collectors fabricated in laboratories [11–15]. As explained in Section 2.5.1,
these existing devices use air as the cladding for TIR to occur which makes the external MOSs
vulnerable in practical usage. Because air has a low refractive index compared to PDMS ($n_{\text{air}} \approx 1.0$ vs. $n_{\text{pdms}} \approx 1.4$) using air as the cladding might simply be an easy solution to improve
TIR functionality in bending. Regardless, PDMS can be used as the cladding for a robust
design in a monolithic fashion since its refractive index can be modified and is explained in
the next section. In conclusion, the properties of PDMS match the key requirements given in
Table 2.3 while also being commercially available with vast documentation. The challenge
is now to create a scalable fabrication method using this material where the time to fabricate
must be greatly reduced for it to be considered for industry applications. Sylgard 184 from
Dow Corning [63] is used in this fabrication research due to availability and faster cure times
compared to other products.

2.6.3 Modifying the Refractive Index of PDMS

It is essential to have the ability to modify or tune the refractive index, $\eta$, of whichever material
has been chosen for a monolithic design and fabrication approach. PDMS is the material of
choice in this research and has a few known techniques to increase its $\eta$, however no techniques
to decrease the $\eta$ were found. Some of these techniques have been applied to the fabrication
of simple PDMS waveguides [55, 71–73] while others are used in applications requiring a
specific tuned $\eta$, such as for volatile organic compound sensing [74] or other biosensor ap-
plications [75]. Four techniques to modify $\eta$ are detailed below where the reason behind an
increase or decrease in $\eta$ can be understood from Sections 2.2.3 and 2.2.5 due to slight changes
in density, material composition, and the dielectric constant, $\epsilon_r$.

Pre-polymer Mixing Ratios

Cai et al. [71] investigated the $\eta$ change in Dow Corning’s Sylgard 184 PDMS [63] due to
changing the mixing ratios of the base and curing agent prior to curing. Sylgard 184 suggests a
base to curing agent ratio of 10:1 by weight. This creates PDMS with a $\eta$ of $\approx 1.422@460$ nm
when cured at 65 °C for 2 hours. Mixing the PDMS pre-polymer at a 20:1 base to curing agent
ratio and curing with the same parameters will create a soft version [65] of PDMS that has a
lower $\eta$ ($\approx 1.417@460$ nm) or mixing it at a 5:1 ratio will create a hard version [65] of PDMS
that has a higher $\eta$ ($\approx 1.424@460$ nm) giving a $\Delta \eta$ of 0.007 which relates to an approximate critical angle ($\theta_{\text{crit}}$) of 84°. They fabricated a simple waveguide using this technique and proved it is sufficient for light guidance with minor bending.

**Curing Parameters**

Chang-Yen et al. [55] investigated the $\eta$ change in Dow Corning’s Sylgard 184 PDMS due to changing the curing parameters: temperature and cure time. They found that at the suggested 10:1 mixing ratio, curing at 50 °C for 1 hour gave a measured $\eta$ of $\approx 1.465@460$ nm and when cured at 150 °C for 1 hour it gave a $\eta$ of $\approx 1.472@460$ nm which also gives a $\Delta \eta$ of 0.007, similar to the mixing ratio difference. Also similar to the previous technique, curing at higher temperatures for the same amount of time creates a slightly harder (higher $E$) PDMS [66]. This technique shows it is important to use the same curing parameters for each PDMS layer when using any other technique, or to properly calibrate for this change in $\eta$ if multiple curing parameters must be used.

**Deep Ultraviolet Irradiation**

Valouch et al. [72] used deep ultraviolet irradiation (DUVI) to create simple waveguiding channels with Y-splitters in Sylgard 184 PDMS. This technique is permanent, stable, and is applied after the PDMS has been fully cured, making it unique from other modification techniques. Low-cost 185 nm and 254 nm Hg-UV-lamps were used with a mask to create the channels with higher $\eta$. 1.5 J/m$^2$ of DUVI increased $\eta$ of PDMS by 0.001 which can guide light without bending. DUVI of PDMS removes carbon and oxygen from the cross-linked polymer chain and prolonged exposure can increase $\eta$ by over 0.04 which approaches the $\eta$ of SiO$_2$ [76]. Unfortunately, Valouch et al. [72] found that prolonged exposure past $\Delta \eta= 0.001$ creates a brittle PDMS which can crack and cause light scattering. Atomic force microscopy on the 1.5 J/m$^2$ irradiated areas also showed a change in height of approximately 50 nm. This technique cannot modify $\eta$ enough for flexible waveguiding without the PDMS becoming brittle. However, the fact that this technique can modify the $\eta$ of specific/complex areas after fabrication could prove useful in future research for creating index-grated MOSs as long as the change in layer height is calibrated for. The DUVI modified MOSs may become slightly brittle, but if they are designed small enough they may still function properly when surrounded/protected by the elastic PDMS.
Adding Nano-particles With a High $\epsilon_r$

The final technique to modify the $\eta$ of PDMS, and the most robust of options, is to dope the material with high dielectric constant ($\epsilon_r$) material such as the oxides of Germanium, Zirconium, or Titanium [74, 75, 77, 78]. These oxide materials are not transparent to light, however incorporating them in a nano-particle form will cause little interaction with most of optical light’s wavelengths (200 – 1000 nm) because their diameters (5 – 70 nm) are much smaller. Therefore, when relatively small amounts of nano-particles are well-dispersed within a medium they essentially become transparent as light will rarely interact with this small particle size. A uniform dispersion of high $\epsilon_r$ nano-particles will increase the effective $\epsilon_r$ of the entire medium which relates to an increase in the $\eta$ of a transparent medium as explained in Section 2.2.5.

Raman et al. [75] increased the $\eta$ of PDMS by dispersing titanium dioxide (TiO$_2$) nano-particles into tert-butyl alcohol, a PDMS-compatible solvent [79]. The solvent mixture was added to PDMS and left to evaporate out of the PDMS matrix as it cured at room temperature, leaving the dispersed TiO$_2$ behind. They measured refractive indices ranging from 1.46 to 1.63 relative to the amount of TiO$_2$ added, but unfortunately did not investigate the new transmittance or mechanical properties. Lee et al. [77] increased the $\eta$ of PDMS by dispersing zirconium oxide (ZrO$_2$) nano-particles into the PDMS matrix via ligand molecule engineering. They found $\eta$ varied from 1.39 to 1.65 simply by increasing the ZrO$_2$ content from 0 to 20.8% v/v and achieved a transmittance of 96% in the visible spectrum, but also did not investigate the new mechanical properties. Motakef et al. [78] increased the $\eta$ of PDMS with SiO$_2$-GeO$_2$ and SiO$_2$-TiO$_2$ nano-particles using a sol-gel technique. They found the SiO$_2$-TiO$_2$-PDMS had the highest increase up to $\eta=1.562$. The transmittance of SiO$_2$-TiO$_2$-PDMS was measured and found a value of 95% starting at the visible range (350 nm). In SiO$_2$-GeO$_2$-PDMS this transmittance started earlier at 200 nm. They also found that large additions of SiO$_2$-X nano-particles caused the PDMS to become brittle and issues occurred when spin-coating thin films with the mixtures.

Little [74] wrote a M.Sc thesis on tuning the $\eta$ of PDMS for label-free optical sensing using several nano-particle based approaches. PDMS-zirconium-oxo and PDMS-titanium-oxo nano-composites were created using a sol-gel synthesis with naphthyl-functionalized PDMS and showed the best results. PDMS-zirconium-oxo were created with 0 – 15 mol % zirconium and yielded refractive indices ranging from 1.4023 ± 0.0002 to 1.4745 ± 0.0002 at 635 nm creating a $\Delta \eta$ of over 0.07. PDMS-titanium-oxo nanocomposites were created with 0 – 30 mol % titanium and yielded refractive indices ranging from 1.4054 ± 0.0004 to 1.5187 ± 0.0009 at 635 nm creating a $\Delta \eta$ of over 0.1. Both techniques showed a linear increase in refractive index with increasing amounts of zirconium and titanium up to 15 and 30 mol %, respectively; beyond which resulted in a brittle and cracked PDMS. Unfortunately, Little [74] did not in-
vestigate the new transmittance, but stated that the films were indeed transparent. Since the sol-gel synthesis and several other incorporation techniques are complicated processes, Little [74] also investigated a very desirable technique to increase the $\eta$ of PDMS using commercially available nano-particle products. Since titanium proved to have the greatest increase in $\eta$ due to its very high $\epsilon_r$ [80], several commercial TiO$_2$ products with hydrophobic surface modifications were purchased for the direct addition into the PDMS pre-polymer or a compatible solvent [79]. Unfortunately, the commercial surface-modified TiO$_2$ nanoparticles were unsuccessful in increasing the $\eta$ of PDMS due to the inability to prepare transparent colloidal solutions. Mixing commercial TiO$_2$ directly into the PDMS pre-polymer or a compatible solvent is a very desirable technique in fabrication due to the ability to easily control the final $\eta$ through simple changes in TiO$_2$ concentrations during the pre-polymer mixing stage, prior to fabrication. Section 3.2.1 discusses attempts at incorporating other commercially available TiO$_2$ products directly into PDMS or compatible solvents, as was suggested by Little [74] in the suggested future work section.

### 2.7 PDMS-Based Fabrication for Large Area Optical Devices

PDMS is predominantly used in microfluidics research [59–61], meaning that most fabrication information with this material is extracted from this field. This includes, but is not limited to: soft-lithography replication methods, pre-polymer preparation, bonding, alignment, and curing. The existing flexible illuminators and collectors [11–15] extracted their fabrication methods directly from microfluidics using similar laboratory-based methods. As mentioned previously in Section 2.5.1 these designs are not robust where MOSs are located on the functional surface and are thus vulnerable. Air is used as the cladding medium in these designs preventing the need for multiple layers of PDMS. This means there is no need to use bonding and MOS alignment techniques, making these single layer designs much easier to fabricate. The limited research on monolithic PDMS waveguides [55, 71–73] have some information on how layers were bonded and aligned, however none of these have MOSs which add additional complexity when fabrication is considered. Also mentioned prior, PDMS has been an unfavourable material to work with at industrial scales due to long cure times and shrinkage issues [69]. This means that key fabrication requirements must be identified and the technique(s) used to achieve each should add as little time to the overall fabrication length as possible while also not compromising the quality or repeatability of the finished product.

The robust illuminators and collectors in this research are a new contribution to science where such relatively complex designs have never been fabricated before. The goal of this research is not only to be capable of accurately fabricating these complex multi-layered mono-
lithic designs, but also to fabricate them in a scalable, robust, and relatively simple manner that may be desirable for potential industry applications. Therefore, by investigating and experimenting with the existing PDMS-based fabrication techniques from the literature in regards to each identified key fabrication requirement for monolithic illuminator and collector design, a combination of techniques have been identified and are presented as a fabrication methodology in Chapter 3.

2.7.1 Micro-optical Feature Creation

There are many techniques available for creating MOSs of different sizes and geometries for illuminators and collectors. The most important requirement for a functional MOS is that its \( \eta \) must be different than the medium with propagating incident light. The \( \eta \) must be higher if refraction is desired, such as with lenses, or \( \eta \) must be lower if TIR is desired. Without this change in \( \eta \) it will be as if the MOSs do not exist. Therefore, all techniques to create MOSs must either modify the \( \eta \) of PDMS in specific locations or allow for a different \( \eta \) of PDMS to fill, surround and bond with potential structural recesses or extrusions.

As explained in Section 2.5.1, the MOSs in this research are required to be internal, which likely adds complexity to their fabrication and alignment. Internal MOS creation can be performed prior, during or after fabrication. Creating internal MOSs after fabrication can be performed with DUVI [72] if the side effects involving brittleness and expansion are calibrated for. Research regarding the types of MOSs which can be created with DUVI is very limited, however simple MOSs such as dots used in light guide plate research [6, 8] appear practical with this method. Creating internal MOSs during fabrication can be accomplished by etching them directly into PDMS [81–83] between layers before bonding them together. Etching of cured PDMS is not as smooth as other commonly etched materials due to the inconsistent cross-linked polymer chains so it may be difficult to achieve optical surface quality with this method. Another potential creation method during fabrication is to supply additional heat to specific locations during the curing process. As detailed in Section 2.6.3 this will further increase the \( \eta \) of those locations slightly and could potentially be used to create simple MOSs such as dots, but may be difficult to control.

Creating internal MOSs prior to fabrication can be achieved through moulding techniques. Arrays of MOSs can be fabricated prior on separate substrates and replicated onto PDMS layers during the fabrication process, after which these layers can be aligned and bonded to make a functional illuminator or collector with internal MOSs. This method of creating MOSs prior to the actual optical device fabrication process is particularly useful for reducing the overall fabrication time since fabricating large arrays of MOSs can become the most time consuming
part of the process. Therefore, the best MOS creation technique for this research is to fabricate master patterns which can be used repetitively in illuminator/collector fabrication.

## Traditional Soft-Lithography Process

Soft-lithography is one of the most widely used pattern replication techniques using elastomeric materials in research. It was developed and well documented by The George Whitesides Research Group [56, 57] in 1998 and has been updated by Rogers and Nuzzo [58] in 2005. The technique is used to mould either an elastomeric material against a rigid master pattern or a rigid material against an elastomeric master pattern. In any case the unique properties of an elastomer are utilized; hence the coined name soft-lithography. By utilizing an elastomeric material, structures with vertical or inner slanted walls can be fabricated. Traditional injection moulding or casting with a rigid metallic master mould using a rigid moulding material requires draft angles to ensure the part can be pulled from the mould without damage occurring. In soft-lithography the unique properties of the elastomer provide a smooth demoulding process without the need for drafted walls, allowing for the intended and potentially complex geometries of features to be replicated. Additionally, de-moulding with an elastomer is less likely to damage small delicate features, such as the MOSs in this research. In microfluidic research complex fluid channels can be easily fabricated using soft-lithography [59–61]. Or in the existing flexible light guide plate literature Lee et al. [11] were able to fabricate upside-down half cone MOSs using the technique.

The most common material used in soft-lithography happens to be PDMS due to its viscoelastic and inert properties. With an inert material, the technique is relatively safe, simple and very cost effective if a master pattern already exists. Simply create a mould, insert the master pattern, and pour the uncured PDMS over it to precisely replicate the desired complex micro-structured pattern. The master patterns can be re-used making this PDMS patterning technique the method of choice for this research since large areas of negative MOSs are much more practical to fabricate on rigid materials used as master patterns. The challenge then becomes the large area MOS fabrication on the actual master patterns used in soft-lithography, which is detailed in Section 2.7.2.

Traditional soft-lithography with PDMS has two main limitations pertaining to the replicated dimensional precision and resolution of micro-structures; both of which have known workarounds. The first limitation is that PDMS shrinks when thermally cured. Woo and Seung [84] experimented with the shrinkage ratios of curing different thicknesses of PDMS at different temperatures. They found that PDMS shrinks by approximately 1% when cured at the recommended 65 °C. With this information micro-structures can be designed to account for the shrinkage induced by the amount of PDMS and curing parameters used. Or another
workaround is that PDMS will not shrink if left to cure at room temperature for over 48 hours. However, this is not ideal for volume manufacturing as it adds considerable time to the overall process. Wong [69] presented a methodology for faster PDMS cure processes without compromising the quality of parts produced. He found there is a gel point where PDMS transitions from a liquid to a solid and the temperature at this point in the curing process has a direct impact on the shrinkage and warpage observed. Therefore, it is possible to reach the gel point at a low temperature in attempt to reduce shrinkage and then increase the temperature afterwards for a full cure. This technique speeds up the overall curing processes and may be a potential solution for volume manufacturing. The second limitation is that PDMS has a difficult time filling small, deep holes due to the pre-polymer being a viscous liquid. This can be solved by diluting the PDMS pre-polymer in a compatible solvent [79] to thin the liquid and have it capable of filling even deep nano-sized holes [85]. Another solution investigated by Con and Cui [86] uses a thin layer of compatible solvent which aids undiluted PDMS to fill nano features down to 100 nm. Ultimately, solutions exist for soft-lithography’s limitations and the technique can be used to replicate any potential MOSs required in illuminator and collector design.

2.7.2 Large Area Pattern Fabrication

There may be billions of MOSs with multiple geometries located within a 1 m² area for illuminators and collectors. This calls for a scalable large area patterning technique with minimal limitations on what types of MOSs are possible. Using soft-lithography does not limit the type of material used to create large area MOS patterns on. This also means that most micro and nano patterning techniques are still available for consideration. Additionally, it is important to note that patterns can be transferred from one substrate to another using soft-lithography, therefore if the negative pattern is not possible to fabricate using a certain technique, but the positive pattern is possible, soft-lithography can be used to invert the pattern as necessary. Gitlin et al. [87] investigated the effects of casting PDMS on a PDMS master pattern and then using the newly patterned PDMS as the next master pattern; repeating several times as an approach to inverse a given micro-structure multiple times. They used a non-texturing release agent to prevent adhesion and found excellent reproducibility and precision with this method.

There are many available patterning techniques to create micro and nano structures on a variety of substrates where covering each technique in detail is outside the scope of this research. Instead, two well-known and standard techniques: photo-lithography and micromachining for fabricating MOSs are briefly explained below and then summarized in Table 2.4. It is important to note that some potential illuminator and collector designs may have many different geometries of MOSs within them and others may have the same repeating MOS geometries.
Therefore, the ideal large area patterning technique should be capable of accommodating for a varied MOS design as well as a repeating one.

Photo-lithography

Photo-lithography is a small-scale patterning technique capable of creating many common MOS geometries such as prisms and pyramids at both micro and nano scales. In fact, due to these capabilities existing literature on flexible and rigid illuminators/collectors research use photo-lithography techniques to fabricate the MOSs on master patterns [4, 8–12]. Photo-lithography uses light to transfer geometric patterns from a photomask to a light-sensitive chemical layer called a photoresist which lays over the main substrate to be modified. Chemical etching is then used to etch the main substrate and create all negative micro-structures simultaneously before the photoresist is removed. The geometries and surface finish created by photo-lithography are limited by the etching process and substrate used. For example, anisotropic wet etching (orientation dependent etching) can be performed on single-crystal materials, such as silicon wafers which are a very common photo-lithography substrate, to create angled negative structures with a perfect optical quality surface finish. The angles, however, are limited to the crystalline structure of the substrate. There exists many other techniques that can be used with photo-lithography to create other geometries such as etching small holes and spin coating a viscous uncured rigid polymer over them to create concave micro-lenses [13]. Photo-lithography is predominantly used in complex integrated circuits, such as the nano-sized transistor arrays in modern central processing units (CPUs). The microfabrication technique sounds like an ideal MOS fabrication technique for this research, however the diameters of the circular silicon wafers used in photo-lithography only range from 23 mm to 450 mm [88] where the fabrication cost greatly increases with diameter. Even at the most expensive 450 mm option, the available area to create MOSs for patterning large area optical devices using photo-lithography is far too small for this research. To actually create large area master patterns using photo-lithography many silicon wafers must be used and then properly aligned in an array, however this is a very expensive option.

Micromachining

Micromachining encompasses many processes by which small microscopic pieces of material are removed from a substrate or stock part in order to achieve a high geometrical accuracy [89]. The main similarity between all types of micromachining is that a very small tool of some kind is precisely guided to remove the desired region of material. End mills, diamond cutters, and

\[^3\] For example, etching a (100) silicon surface will create slanted walls with a precise angle of 54.7°
lasers are examples of different tools used in micromachining. With each tool, micro-structures are formed in succession allowing for different geometries to be fabricated during the same overall process by utilizing tool changes. Brinksmeier and Preuss [90] discuss several micromachining techniques to create different geometrical structures with optical quality surface finishes which could potentially be used for illuminator and collector designs. Micromachining can be used to create most common types of MOS geometries, however the size of MOSs are typically in the micrometre range and rarely approach the nanometre range due to physical constraints of small tools. Due to the subsequent micro-structure fabrication, micromachining can take a very long time to fabricate a large area pattern of MOSs. Fortunately, to make up for the lengthy fabrication times, micromachining does not have an area limitation. Even if the machine used to precisely guide the micro-tools hits one of its planar limits, the stock piece can be repositioned and accurately re-aligned to the planar position of a previous micro-structure to continue the patterning process.

**Comparison: Photo-lithography vs. Micromachining**

The main requirement for MOS fabrication in this research is to be capable of patterning a large area. Potential illuminator and collector designs may require repeating MOSs where small-area patterning techniques can be used with other techniques which repetitively apply the same pattern to a substrate such as roll-embossing. However, it is desirable within industry to have a patterning technique in-house that is as flexible as possible for easily prototyping new large area designs. Table 2.4 below summarizes the two most common MOS fabrication techniques where micromachining is preferred due to its scalability and flexibility. Section 3.2.2 in the next Chapter details the specific micromachining techniques used in the fabrication of master patterns for this research. Micromilling with a computerized numerical control (CNC) machine was used due to its availability, low cost and scalability potential for large area pattern fabrication.

**2.7.3 Controlling Layer Thickness**

Section 2.4.4 explained how important it is to control the thickness of layers for MOSs to function properly. Existing literature using PDMS have some techniques for creating thin layers and controlling thickness. The best techniques for this research are ones capable of controlling a range of consistent thickness over a large area and may help with creating internal MOSs.
Table 2.4: Comparison of photo-lithography vs. micromachining for large area pattern fabrication

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Photo-lithography</th>
<th>Micromachining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall fabrication time</td>
<td>Relatively short - capable of removing material for all micro-structures simultaneously</td>
<td>Lengthy - micro-structures are fabricated subsequently</td>
</tr>
<tr>
<td>MOS geometries possible</td>
<td>Etching techniques and different substrates exist to create most with additional help from other micro-fabrication processes</td>
<td>Many tools and techniques exist to create most</td>
</tr>
<tr>
<td>Typical size of MOSs</td>
<td>Nanometre scale</td>
<td>Micrometre scale</td>
</tr>
<tr>
<td>Area constraint per process</td>
<td>Limited to 450 mm diameter wafers</td>
<td>No limit assuming sufficient machine space</td>
</tr>
<tr>
<td>Cost</td>
<td>Very expensive with increasing area</td>
<td>Constant machine running cost regardless of area</td>
</tr>
</tbody>
</table>

**Traditional Spin-coating**

Spin-coating is the traditional thin film technique used in laboratories. It is often used in microfluidic mould fabrication [59, 60] and even in the fabrication of existing PDMS illuminators [11]. Thin films are achieved by pouring a viscous liquid, uncured PDMS in this case, onto a disk and then spinning the disk rapidly so the viscous liquid is pushed to the outer edges by centrifugal force. Parameters such as viscosity, friction, spin rate and time accurately control the thickness of the resultant thin film upon the disk. This technique can be applied over master patterns to fill cavity features and create micro-structures on the bottom of the thin film. Spin-coating is capable of creating very thin films, Koschwanez *et al.* [91] investigated the thickness of PDMS thin films created in relation to spin rate and time. They found that at a spin rate of 6000 RPM, pure PDMS could be spun to a thickness as small as 4 µm after 60 minutes of spin time. They also discovered that exceptionally thin films could be created by diluting PDMS in a compatible solvent [79] to decrease the viscosity. Tert-butyl alcohol was used as the solvent due to its minimal swelling with cured PDMS and left to evaporate out while the PDMS cured. Films as thin as 1.5 µm were created with an 83% solvent mixture at 6000rpm.

Traditional spin-coating is not used to cover a large area, which is why its often seen only in laboratories. This is likely due to the large centrifugal forces that occur if the disk were to be
much larger, potentially causing the thin film of PDMS to become less consistent the further it is away from the axis of rotation.

**Open Cavity Moulding**

The thickness of a layer can be controlled by calculating the volume of PDMS required within a region, such as an open mould, then pouring it over a master pattern to achieve the desired layer thickness. This is typically performed using the mass of PDMS poured where the density is known. This technique is dominant in the fabrication of PDMS microfluidic devices [59–61] due to the ability to use solvents to thin the PDMS pre-polymer and fill small, deep micro-structure cavities. It has also been used in the fabrication of existing illuminators through casting upon a diffusing pattern [12, 14]. Having an open mould allows the solvent to evaporate out while the PDMS cures, which can also be used to create thin films. Additionally, if a solvent is not used an open cavity mould allows for any potential bubbles to escape from the viscous pre-polymer and can be accelerated via vacuum degassing. To further control the thickness of layers in open cavity moulding, especially when a large area is required where surface tension may affect thickness uniformity, a squeegee or doctor’s blade [25] can be used to remove excess polymer or to uniformly distribute it over the mould to the desired thickness. Open cavity moulding is a simple method to pattern the bottom surface of PDMS where additional techniques exist for large area applications.

**Closed Thin Cavity Moulding**

Closed thin cavity moulding is a technique where liquid pre-polymer is inserted into a thin featured cavity. In this technique, the thickness of the layer is already pre-set during the mould’s design and fabrication. Closed cavity moulds are not found in existing illuminator and collector literature, perhaps due to the difficulties of inserting a pure material into the thin cavity while also filling the micro-structure features, since a thinning solvent cannot be used. The only similar technique found was an attempt by Shih et al. [13] to close their open cavity mould for additional thickness control after the PDMS had been degassed and allowed to fully fill their MOS pattern. Actual closed thin cavity moulding, however, could potentially allow for micro-structures to be patterned on the top and bottom surfaces of the layer when the PDMS is inserted. Patterning PDMS on both surfaces of a layer is desirable in this research for creating internal MOSs in certain designs. Due to the lack of existing literature, Section 3.3.2 describes a few quick experiments using injection and suction on a 0.4 mm thin mould cavity with simple micro-drilled features to understand why open cavity moulding and spin-coating have been preferred for thin designs. In both cases it was very difficult not to create gas bubbles
as the PDMS lapped over itself and failed to fill several MOS features, creating an impure material that would be subject to light scattering. It was later found that in microfluidics research, Mazzeo [92] successfully used centrifugal force to insert PDMS pre-polymer into a closed thin mould cavity with a minimum thickness of 50 µm. Section 3.3.2 describes this novel centrifugal casting process which was capable of filling small microfluidic features while simultaneously degassing the viscous liquid, solving the injection and suction issues which occur in closed thin cavity moulding.

2.7.4 Bonding and Alignment of Multiple Thin Layers

The design of monolithic PDMS illuminators and collectors requires multiple layers of different η with MOSs present between them to achieve a robust design for practical applications. This will require a method to firmly bond and accurately align layers. Several techniques exist to bond PDMS to PDMS, however only the techniques which do not require an intermediate substance between layers are applicable to this research. For example, Koh et al. [93] uses a strong acid (Piranha solution) to bond PDMS-PDMS layers. This acid solution creates a thin film of a different η between layers which will affect TIR and thus the overall optical device functionality. Therefore, only the techniques which temporarily modify the two PDMS surfaces specifically for bonding can be considered for this research. Eddings et al. [94] investigated the bond strength of five different PDMS-PDMS bonding techniques, three of which are applicable to this research: Oxygen Plasma, Corona Discharge, and Partial Curing. Oxygen plasma bonding is the standard bonding technique used in microfluidics research to promote adhesion between PDMS and other materials, even PDMS itself. It uses a plasma cleaner to modify the surface properties of PDMS with oxygen, ultimately increasing the surface energies through Si-OH groups to increase the bond strength of PDMS’s hydrophilic surfaces. Corona discharge is a similar technique to oxygen plasma which uses high voltage discharge to create plasma in the air above the surface (i.e. also oxygen) which also increases the surface energies through Si-OH groups, but to a lesser degree. Finally, partial curing is a technique where PDMS is not completely thermally cured, yet has been cured enough to solidify; afterwards, more uncured PDMS is poured on top of this partially cured surface where some cross-linking of polymer chains will still occur at this interface. Eddings et al. [94] found that partial curing had the highest bond strength, followed by oxygen plasma and then corona discharge.

The accurate alignment of thin PDMS layers is a difficult challenge, but is necessary for illuminator and collector functionality. If two layers are fabricated separately and require MOSs to be present between them, then one layer must have a negative pattern of MOSs while the other must have the positive, yet inverse-geometrically identical, MOS pattern. Precise align-
ment of such layers is crucial as a misalignment might create gaps between MOSs, thus changing the affective $\eta$ of them. Since no existing PDMS-based illuminators and collectors [11–15] are more than a single PDMS layer, the alignment techniques are extracted from microfluidics literature. Jo et al. [95] achieved an alignment accuracy of 15 $\mu$m using a manual method under a microscope and Woo and Seung [84] achieved an alignment accuracy of $<10$ $\mu$m by adding an align key and hole to their two layers. These alignment accuracies are often sufficient for microfluidic devices, however in certain collector designs, such as the lens-pyramid design previously illustrated in Figure 2.8, may require a more accurate alignment. Yang et al. [96] thoroughly investigated the bonding of PDMS-PDMS layers via corona discharge and mention that the bonding technique allows for PDMS layers to be peeled and re-aligned for up to an hour after corona treatment, which may help improve accuracy through multiple attempts. Other potential techniques for alignment might exist such as utilizing light through lens MOSs to align with a below layer, or the positive and negative MOSs between layers could facilitate alignment in a similar manner to the key and hole alignment by Woo and Seung [84]. A different approach however, the one discussed in Chapter 3, is to utilize the partial curing technique to bond layers without the need for alignment. When the partial curing technique to bond layers is used with a patterned surface, this surface essentially becomes the new master pattern for the subsequent layer where the alignment of more MOSs is achieved by simply pre-aligning the master patterns within the mould cavity.

2.7.5 Fabrication Preparation and Post-Processing

In the fabrication of almost any complex device, there may be many overlooked considerations that may affect the overall quality of the finished product. This Section will supply some insight from existing literature on some of the more obvious considerations that may be apparent before the experimentation phase. It is important to note, however, that many potentially overlooked considerations may still exist. In this research, the fabrication methodology presented in Chapter 3 has been designed for scalability, but as the fabrication area becomes larger new issues might still arise. Section 5.3 in Chapter 5 attempts to provide insight with possible solutions for potential issues that might arise as the area of the presented fabrication methodology increases.

Bubble-free Product

PDMS pre-polymer is a thick liquid with a viscosity of $\approx 3.5$ kg/m·s [63] and thus has issues with trapped gas bubbles prior to curing. Additionally, since PDMS is supplied as a base and curing agent to be mixed, even the act of mixing these two compounds together creates many
bubbles. Once the PDMS is cured any bubbles trapped in the pre-polymer will end up in the final product, which makes the product insufficient for light propagation due to the scattering affects described in Section 2.2.3. Therefore, all gas bubbles must be completely removed prior to curing. There exists a few techniques to aid the escape of gas bubbles formed after mixing PDMS by increasing the buoyant forces that the viscous liquid exerts upon them. The buoyancy force acting in the opposite direction of gravity, $g$, of a submerged body [97] is given by:

$$F_{\text{buoyancy}} = \rho_f V_b g$$  \hspace{1cm} (2.15)

where $\rho_f$ is the density of the fluid and $V_b$ is the submerged body’s volume.

Vacuum degassing is the most common and standard technique for degassing PDMS. It is used in microfluidics [59–61] and existing illuminator and collector literature [14, 15] where open cavity moulds are placed in a vacuum chamber. The mixed and bubble-ridden PDMS becomes subjected to negative pressure which causes the trapped bubbles (previously at atmospheric pressure) to expand, increasing their volume and in turn also increasing the exerted buoyant force in Eq. 2.15. Vacuum chamber degassing can take a lengthy amount of time to fully remove all bubbles depending on the initial number of bubbles, the vertical distance of bubbles from the surface, and wall friction effects. It can take anywhere from 30 min to 2 hrs to fully degas an open cavity mould.

A second technique, previously mentioned in Sections 2.7.1 and 2.7.3 is to use a compatible solvent for thinning PDMS to remove bubbles and then allow the solvent to evaporate out. This reduces the drag force upon a rising bubble, instead of changing the buoyant force. The drag force of a bubble with diameter $D$ moving at velocity $v_b$ can be modelled according to the Hadamard-Rybczynski relationship [98] which is given by:

$$F_{\text{drag}} = 3\pi D \mu_f v_b \frac{2\mu_f + 3\mu_b}{3\mu_f + 3\mu_b}$$ \hspace{1cm} (2.16)

where $\mu_b$ is the dynamic viscosity of the air within the bubble and $\mu_f$ is the viscosity of the fluid. It can be seen from Eq. 2.16 that a decrease in fluid viscosity with the addition of a solvent will reduce the drag exerted upon a rising bubble, thus allowing bubbles to escape quicker. This technique is more often used for filling extremely small features [85], but can also be used to remove bubbles. The thickness of PDMS-solvent will dictate how long it takes for the solvent to fully evaporate out, so it is wise to only use this technique for thin components, which may also be why it is typically used in conjunction with traditional spin-coating (Section 2.7.3).

A third and final technique, which is capable of rapidly degassing PDMS, is to apply centrifugal force to greatly increase the buoyancy force [99]. Centrifugal force essentially adds a large artificial gravity component to Eq. 2.15 which greatly increases $F_{\text{buoyancy}}$, forcing bubbles
towards the axis of rotation. High RPM lab centrifuges can degas PDMS in as little as two minutes [100].

Through experimentation, it was found that regardless of the technique used to degas PDMS prior to filling a simple mould cavity, new bubbles would always form from the PDMS lapping over itself or failing to initially fill small features, such as MOSs. This explains why the lengthy vacuum chamber degassing is preferred in the literature due to the ability to perform the technique while the PDMS is already within an open cavity mould. Potential moulding solutions exist to solve this, such as continuously pushing or pulling pre-polymer through a closed mould cavity until all the newly formed air bubbles have been sent out. Such solutions may be wasteful, inconsistent, and could even leave very small bubbles which are not visible, but could expand and form during thermal curing. A potentially better solution mentioned in Section 2.7.3, is to apply centrifugal force to a closed thin mould cavity which not only aids in filling the mould, but can also be used to completely remove bubbles from the cavity due to buoyancy and diffusion effects [101].

**Thermal Curing**

To decrease typical fabrication times with PDMS, thermal curing will be required. Section 2.7.1 briefly explained that Wong [69] investigated rapid thermal curing of PDMS for industrial applications. To reiterate, he found there exists a gel point where PDMS transitions from a liquid to a solid and the temperature at this gel point directly affects the amount of shrinkage induced by the polymer. Wong [69] used 85 °C until just past the gel point, then rapidly increased the temperature to 135 °C to produce a part in a fifth of the manufacturer recommended time. Even faster cure times may be achievable with post-gel point temperatures up to 200 °C before reductions in mechanical strength may occur [67]. Considering the potentially high curing temperatures, a mould material which can withstand these temperatures is required. Additionally, since PDMS already undergoes slight shrinkage, it is wise to choose a mould material with a low coefficient of linear thermal expansion (CLTE) in an attempt to prevent additional PDMS quality issues. Table 2.5 lists a few common mould materials with their CLTE and melting points [102, 104]. The polymers listed show relatively low melting points with high CLTE and thus should be avoided for thermal curing. For example, poly(methyl methacrylate) (PMMA), a common master pattern material [13, 66], has a melting point of 160 °C where softening will also occur before this temperature. Therefore, this material should not be used as master

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4 Liu et al. [67] did not investigate this affect with a lower gel point transition temperature. The 200 °C at the gel point may have been the cause for reduction in mechanical strength. Further investigation is required to see if high temperatures past a low gel point transition affect mechanical strength.

5 Sourced from [102]

6 Metals and polymers sourced from [103] and [104], respectively
patterns in high temperature applications. Metals, such as steel and titanium, show promising properties for use as mould and master pattern materials with very high melting points and low CLTE. Ultimately, many additional considerations such as cost and machining should be a part of mould design, however high melting points and low CLTE are very important for decreasing PDMS-based fabrication times through rapid thermal curing while also preserving quality. Combinations of materials should also be considered. For example, if cost is of low concern then titanium with a thin film coating of polytetrafluoroethylene (Teflon) will not melt nor expand much at 200 °C and may help aid the removal of PDMS from the mould with Teflon’s low coefficient of friction and hydrophobic properties.

Table 2.5: Potential mould materials with melting points and coefficients of linear thermal expansion

<table>
<thead>
<tr>
<th>Material</th>
<th>CLTE ($10^{-6}$ m/m·K)</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>22.2</td>
<td>≈ 660</td>
</tr>
<tr>
<td>Brass</td>
<td>18.7</td>
<td>≈ 950</td>
</tr>
<tr>
<td>Bronze</td>
<td>18.0</td>
<td>≈ 925</td>
</tr>
<tr>
<td>Copper</td>
<td>16.6</td>
<td>≈ 1084</td>
</tr>
<tr>
<td>Magnesium</td>
<td>25.0</td>
<td>≈ 650</td>
</tr>
<tr>
<td>Steel</td>
<td>12.0</td>
<td>≈ 1370</td>
</tr>
<tr>
<td>Titanium</td>
<td>8.6</td>
<td>≈ 1670</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>75.0</td>
<td>≈ 160</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>70.2</td>
<td>≈ 265</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>200.0</td>
<td>≈ 137</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>100.0</td>
<td>≈ 327</td>
</tr>
</tbody>
</table>

De-moulding of MOSs and Surface Treatments

A very important step in any moulding process is the removal of parts from a mould. The de-moulding process is crucial in preserving the intended quality of parts produced. In illuminator and collector fabrication this becomes one of the most important steps due to the existence of many small MOSs which may become damaged with improper removal. Damaged MOSs can compromise the functionality of the entire device. As explained in Section 2.7.1, PDMS’s elastomeric properties allow it to easily peel off a complex featured master pattern. However, this is assuming there is minimal adhesion between the PDMS and master pattern surface. If
adhesion exists, MOS features may stretch and break during peeling, or the amount of strain induced on the full PDMS device while peeling may cause permanent deformation. Additionally, if de-moulding from a partially cured PDMS surface (Section 2.7.4) the polymer will be much softer, so the potential for damage during removal is increased. There are two key techniques to prevent damage during the de-moulding step. The first technique is to apply a thin anti-adhesion coating layer, often called a release agent, to the mould surfaces. These coatings lower the mould’s surface energy to prevent the PDMS from sticking. Silane anti-adhesion layers are the most commonly used release agents in PDMS fabrication [59, 81, 86, 105]. These release agents are typically applied with vapour deposition when SU-8 or PDMS master patterns are required and last for a few soft-lithography replications. Friend and Yeo [59] suggest exposing SU-8 master patterns to the vapour of dimethyloctadecylchlorosilane in a vacuum to create a thin self-assembled anti-adhesive monolayer. Chen et al. [81] use (tridecafluoro-1,1,2,2,6,6-hexafluorohexyl)-1-trichlorosilane on PDMS master patterns while Con and Cui [86] and Zhang et al. [105] use trichloro (1H,1H,2H,2H-perfluorooctyl)silane on SU-8 and PDMS master patterns, respectively. Other types of anti-adhesion layers have been used, such as hydroxypropylmethylcellulose used by Gitlin et al. [87] on PDMS patterns where they found the contact angle of water droplets displayed similar hydrophobicity as plain PDMS. When a material such as a rigid polymer is used as a mould or master pattern, silane or solvent-based anti-adhesion layers should be used with caution as they can cause unintended chemical interactions which could lead to cracking or warpage depending on the polymer-agent combination. An alternative technique which is safe with all mould materials is to apply a thin coating of detergent molecules. Chang-Yen et al. [55] found that a detergent-based release agent on SU-8 moulds performed better than the common silane treatments. Silanes can be hazardous and expensive, but detergent-based release agents are cost-effective and safe to handle which may prove useful for prototyping.

The second technique to aid the de-moulding process is to simply use an elastomer as the master pattern. When a rigid master pattern is removed from a surface, a temporary negative pressure is induced which essentially acts as suction upon MOSs, potentially damaging them. In traditional soft-lithography the careful peeling of a PDMS master pattern already helps prevent damage on the patterned surfaces due to PDMS’s viscoelastic properties. Gitlin et al. [87] also showed excellent reproducibility when transferring micro-patterns from PDMS to PDMS multiple times. Therefore, an elastomeric master pattern, which could consist of PDMS, can be carefully peeled from a PDMS surface and will greatly reduce the strain upon small features. Additionally, this technique is also useful for inverting complex MOSs. Lee et al. [11] use this technique in combination with a silane monolayer to invert their upside down half-cone MOSs in their illuminator fabrication due to the large reduction in de-moulding strain. Regardless of
technique(s) used, the PDMS de-moulding process must be effective in preventing damage of MOSs and thin waveguiding layers.

2.8 Concluding Remarks

This chapter has presented a very thorough overview of light, waveguiding, illuminators, collectors and PDMS-based fabrication methods to create a solid foundation of knowledge for developing a new fabrication methodology. Many elements are present in the robust design and fabrication of illuminators and collectors. Internal MOSs utilizing a monolithic design with flexible materials has not been achieved in current research. To achieve such a contribution to science using PDMS, a combination of known fabrication techniques extracted from many areas of research with a new outlook is required. The discovery of the fabrication methodology presented in the next chapter was only possible through continuous experimentation and tinkering. Many experiments and fabrication iterations failed, however there were certain aspects of each iteration that proved successful, eventually building into a full fabrication methodology. Appendix B briefly summarizes each iteration where gas bubbles were a continuous issue until it was discovered that the centrifugal force used to quickly degas the PDMS pre-polymer before each experiment could be used to fill thin mould cavities while also simultaneously removing bubbles; this lead into the work done by Mazzeo and Hardt [70] in microfluidics.
Chapter 3

Proposed Fabrication Methodology

3.1 Introduction

The goal in this research is to create a scalable methodology for fabricating robust illuminators and collectors with industry potential. More importantly, there are key aspects of illuminator and collector design described in Section 2.5, some of which are new to science and may be difficult to fabricate. These key aspects are: monolithic design, internal micro-optical structures (MOSs), and multiple thin polydimethylsiloxane (PDMS) layers. To develop a fabrication methodology which implements these key aspects, many experiments involving PDMS-based fabrication were necessary. Appendix B details several of these experiments where soft-lithography moulds were tested and design iterations were made. In these experiments, the most common issue was air bubbles appearing in the final PDMS product. In microfluidics literature [59–61] and even in existing flexible illuminator/collector literature [14, 15] this was solved by placing an open mould cavity in a vacuum chamber and waiting anywhere from 30 minutes to over an hour for bubbles to escape the surface. This lengthy degassing method would not be suitable for industry potential or rapid fabrication. Therefore, a new approach extracted from the work of Mazzeo and Hardt [70] was necessary which brought many other positives to thin-layer closed cavity moulding.

The proposed fabrication methodology introduces a new look at multi-layered PDMS-based fabrication. It combines the most robust fabrication techniques from Section 2.7 to create a rapid, robust and effective methodology. Soft-lithography, closed thin cavity moulding, partial curing, and centrifugal casting are all combined to create an effective and scalable fabrication methodology for developing multi-layered large area PDMS optical devices. Together, these techniques allow for a monolithic design with internal MOSs that is built layer-by-layer from the bottom up. It is important to note that there are many factors involved in the optimization of this methodology, however the working proof of concept presented in Chapter 4 proves
the feasibility of this methodology.

This chapter explains, illustrates and details the ideal approach to this proposed fabrication methodology. Section 3.2 explains essential requirements for working illuminator and collector designs which are not necessary towards the overall methodology proof of concept and thus are beyond the main focus of this research. These requirements, however, are present in existing literature so it is important to detail them and discuss how they can be implemented into this fabrication methodology. Sections 3.3 and 3.4 detail the proposed fabrication methodology and its potential limitations. Finally, Section 3.5 discusses the contribution to science regardless of industry application and concluding remarks are presented in Section 3.6.

### 3.2 Essential Aspects of a Functional Design

To create robust monolithic waveguiding sheets with internal MOSs there are a few essential aspects that are necessary for a fully functional and efficient design. These requirements, however, are not essential for the actual fabrication of the product, and only pertain to the efficiency and functionality of the finished product. By using different techniques which are much simpler to achieve, but have a similar outcome, it is still possible to prove a working fabrication methodology through a proof of concept or feasibility study. The next Chapter uses these simpler techniques, however it is still important to show that the ideal techniques to create the most efficient and functional waveguide sheets are still quite possible and exist in current literature, so that they may be implemented in at a later time during a continuation of this vast research project. For example, a research and development team with several members from different backgrounds would be capable of implementing the following aspects and optimizing the methodology presented in this chapter.

#### 3.2.1 Increasing PDMS Refractive Index With Nano-particles for Fabrication

Section 2.6.3 described several techniques to increase the refractive index, \( \eta \), of PDMS which is required for a functional monolithic design utilizing total internal reflection (TIR). A higher \( \Delta \eta \) between mediums (core/cladding) or incident upon MOSs gives a larger critical angle, \( \theta_{\text{crit}} \), thus allowing for more bending and flexibility before light escapes unintentionally. The technique which resulted in the greatest increase in \( \eta \) of PDMS was to add nano-particles with a high dielectric constant, \( \epsilon_r \). Little [74] and Raman et al. [75] found that titanium dioxide \((\text{TiO}_2)\), with a very high \( \epsilon_r \) of 86-173 [80] increased the \( \eta \) of PDMS by over 0.1. The procedure by Raman et al. [75] did not appear overly complicated and experiments were performed to re-
produce the work. Rutile TiO$_2$ nano-particles with an average diameter of 21 nm and tert-butyl alcohol were purchased from Sigma-Aldrich\(^1\). Figure 3.1 shows the final results after several experiment iterations. The instructions from Raman et al. [75] were followed, weighing and sonicating as advised, yet the result was always an opaque mixture of aggregates. The ”S” on the left in Figure 3.1 is the final attempt where a small amount of transparent detergent was added hoping that the polar and non-polar detergent molecules would solve aggregation. This proved unsuccessful overall, however the TiO$_2$ particles never settled to the bottom of the tert-butyl alcohol when left untouched over time as they did without the added detergent. Raman et al. [75] synthesized their own TiO$_2$ nano-particles while the ones used in this experiment were purchased. The technique used to synthesize their nano-particles may have created particles with different surface properties which created transparent colloidal solutions in tert-butyl alcohol. Additionally, Raman et al. [75] had never investigated the overall transmittance of their TiO$_2$-PDMS and used very thin films which would appear transparent. Regardless, the experiment could not be reproduced to create transparent colloidal solutions and was attributed to inexperienced user error without a chemical background.

Figure 3.1: Tert-butyl alcohol and 21 nm TiO$_2$ nano-particles result. The ”S” on the left had a small amount of detergent added to see its effect. Aggregates formed in both mixtures, making them opaque.

Little [74] had mentioned that it might be possible to purchase commercial surface-treated TiO$_2$ products and directly add them into the PDMS pre-polymer or a compatible solvent [79]. This is a very desirable technique for increasing the $\eta$ of PDMS for this research, especially for an inexperienced user. Commercial products could be purchased, and weighed out to increase the $\eta$ of PDMS by a the required amount. Since Little [74] mentioned that other surface-treated commercial products and solvents should be tested in the future work Section, a similar experiment was performed. A pre-synthesized transparent colloidal solution of 4−8 nm hydrophobic-

\(^1\) Sigma-Aldrich product website: [106]
coated TiO₂ nano-particles in methyl-ethyl-ketone (MEK) was purchased from PlasmaChem GmbH². MEK (also known as butanone) is a compatible solvent with PDMS which has a very low swelling ratio [79]. It had seemed this may be the ideal commercial product for simply adding it to the base of Sylgard 184 PDMS pre-polymer and allowing the MEK to evaporate out, leaving TiO₂ nano-particles behind where the curing agent could then be added to create PDMS with high η. Figure 3.2 shows the final experimental results. Unfortunately, the product from PlasmaChem solidified and became opaque a few days after arrival. Figure 3.2 shows the resultant product³ after advice from the supplier was followed. The left image shows an opaque mixture after more MEK was added and sonicated. The right image shows that all the TiO₂ nano-particles had unfortunately become aggregates after placing the mixture in a centrifuge for 10 minutes at 8000g.

Figure 3.2: Methyl-ethyl-ketone (MEK) and TiO₂ result. Original product became opaque and solidified, therefore additional MEK was added and sonicated, as advised by the supplier (left). After failure to create another transparent colloidal solution was observed, the product was centrifuged at 8000g for 10 minutes where it appears all TiO₂ had become aggregates (right).

To observe if the hydrophobic-coated TiO₂ nano-particles may still work in the PDMS matrix, the remaining original solidified product was heated which resulted in an opaque liquid. Figure 3.3 shows the result after allowing the MEK to evaporate from the PDMS base in a

² PlasmaChem product website: [107]
³ Background removed with image manipulation software. The left image also appears green due to the lighting in a biochemical lab.
fume-hood for 48 hours and then adding the curing agent to cure the PDMS. The result was an opaque sample of PDMS which could not be used for waveguiding.

Figure 3.3: The original methyl-ethyl-ketone (MEK) and TiO$_2$ product was heated until it liquefied and then added to the base of Sylgard 184 PDMS, regardless of opaqueness. As expected, the resultant cured PDMS after allowing the MEK to evaporate out was also opaque.

Section 5.3 describes other commercial TiO$_2$ products with surface modifications which could potentially work for increasing the $\eta$ of PDMS. Due to time constraints, further experiments that involved increasing the $\eta$ of PDMS with TiO$_2$ nano-particles were abandoned. Instead, the proof of fabrication methodology experiments presented in Chapter 4 opted for the pre-polymer base/agent ratio technique used by Cai et al. [71] to increase the $\eta$ by just 0.007. Using a non-ideal technique to increase the $\eta$ of PDMS still showed some functionality while also verifying the fabrication methodology. If a working procedure to add commercial TiO$_2$ nano-particles to PDMS is discovered, it can be added to this research when preparing the polymer for the core layer(s).

3.2.2 Pattern Fabrication

The functionality and efficiency of illuminators and collectors is directly related to the quality of the MOS pattern present in the device. Section 2.4.3 and 2.7.2 explained the importance of MOSs with examples and how to fabricate them over a large area. To reiterate, the geometries, spacing, and surface finishes all affect the overall functionality of the fabricated device. It is important to note that smaller MOSs are often better as they are less likely to interact with propagating light through the core layer in an unintended way. Smaller MOSs allows for more to be packed into an area, resulting in better uniformity. In this research, micromachining has been chosen as the pattern fabrication technique due to its scalability and versatility for large
area production. Other techniques for even larger areas can be used with micromachining if patterns have repeating MOSs such as roll embossing.

Small MOSs are better, however they can be very time consuming and thus expensive to fabricate using full-sized micromachining processes. Therefore, in the next Chapter larger MOSs are fabricated with readily available traditional computerized numerical control (CNC) milling machines as to reduce cost and time for the proof of concept using this fabrication methodology. Micro-tools are used with the CNC machines to fabricate patterns on poly(methyl methacrylate) (PMMA). These micro-tools have been polished to supply an optical surface finish on soft plastics, however the RPMs of traditional CNC machines cannot reach the required amount for these tool diameters, so the machine must be run much slower and will not produce the ideal surface finish that the tools are capable of. Regardless, the resultant MOS patterns produced still display illuminator functionality and verify the fabrication methodology.

Using micromilling as opposed to other micromachining techniques limits the geometries of MOSs that can be created. For example, the pyramids or cones illustrated in Section 2.4.3 which redirect light to all edges of a collector are difficult to fabricate with a perfect pointed tip using micromilling. However, collector designs can be modified to work with micromilling techniques. Instead of a pyramid or cone, a simple wedge can be used to redirect light to a single edge of the collector. Figure 3.4 illustrates an example fabrication approach for creating wedge MOSs with simple CNC micromilling. The left illustration shows how a stock part can be angled to some degree where a flat end mill can be touched into the part to create an array of small wedges. The right illustration shows a resultant wedge MOS after soft-lithography is performed. The dimensions of this wedge are equivalent to the inclination of the stock part, the tool diameter used and the short distance the tool was touched into the part.

![Figure 3.4: Fabrication approach to creating a wedge MOS. The flat end mill is touched into the angled stock part (left) to create a replicated wedge of the same angle and dimensions of the end mill used (right).](image)

An ideal pattern fabrication approach would utilize the many techniques which encompass micromachining [90] to create complex patterned arrays of MOSs. The geometries of
MOSs would be designed and fabricated to be as small and accurate as physically possible to improve functionality and efficiency. This process may be time consuming and expensive, however by utilizing soft-lithography the master patterns may be used a number of times for each design. Furthermore, to go above and beyond, large arrays of patterned silicon wafers from photolithography are also a possibility for nano-sized MOSs.

### 3.2.3 Embedded Light Source in Illuminators

Due to the $\Delta \eta = 0.007$ and pattern feature size constraints described above, a three layer illuminator design was chosen as the large area waveguide sheet to fabricate for the proof of concept presented in Chapter 4. A practical illuminator requires an edge-light source. The illuminators in current literature [11, 12, 14] have an edge-light source, however they are also rigid which limits the overall flexibility of each device. To solve this issue, it was found that flexible light emitting diodes (LEDs) strips could be embedded directly into PDMS prior to curing. Figure 3.5 shows the result of a proof of concept experiment where a readily available LED strip is set into a thick cast layer of PDMS with a generic dot-illuminating pattern. This negated the need for fixing a light source to the edge and ensuring as much light as possible actually enters the core layer. Additionally, thinner, edge illuminating LED strips can also be embedded strictly within the core layer to allow for flexibility and is presented in Chapter 4 as the fabricated illuminator’s light source. Further experiments involving the durability and flexibility of this technique are required, however this proof of concept shows that edge-sources of light may be embedded directly into PDMS during fabrication.

### 3.3 Proposed Build-By-Layers Fabrication Method

Building layers of PDMS from the bottom-up is the essential approach for the creation of internal MOSs. As Section 2.5.1 described, internal MOSs in illuminators and collectors creates a robust design since these small, fragile features are inherently protected by the outer layers. To fabricate from the bottom-up several PDMS-based fabrication techniques from literature had to be combined to develop an entirely new methodology. The key techniques used are: closed thin cavity moulding, centrifugal casting, elastomeric master patterns, and the partial curing technique which are all detailed in specific regards to this methodology in the following sections.

Figure 3.6 illustrates and details the proposed build-by-layers fabrication methodology. First (a), a thin mould cavity with a pre-set thickness for the layer is set-up and attached to

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4 Section 4.3 explains why an illuminator was chosen over a collector.
Chapter 3. Proposed Fabrication Methodology

Figure 3.5: Proof of concept: A LED strip is embedded into PDMS. Since PDMS is an insulator the LEDs are still functional and light transmits directly into the PDMS medium for propagation.

a spindle. An elastomeric master pattern is inserted on the top, or even the bottom, depending on the required design. Mixed PDMS pre-polymer of refractive index $\eta_1$ is poured into a loading chamber in preparation for the next step. Next (b), the spindle with attached mould is initiated and ramped up to several RPMs. As the mould cavity spins around the axis of rotation, the PDMS in the loading chamber is pulled into the thin mould cavity by centrifugal force and fills any small features. The increase of artificial gravity within the mould cavity pushes gas bubbles towards the axis of rotation and smaller gas bubbles dissolve into the solution. Then (c), after a sufficient amount of spin time necessary to remove all bubbles, the loading chamber is closed off and the spindle is stopped. Heat is then applied to the mould for a partial thermal cure of the current PDMS layer. Next (d), the mould is then removed from the heat and the top is removed. The elastomeric master pattern is carefully peeled from the partially cured surface, revealing the replicated pattern. Finally (e), additional wall thickness equal to the subsequent layer’s thickness is inserted and the top is added with a new elastomeric master pattern. The loading chamber is re-opened and new PDMS pre-polymer of refractive index $\eta_2$ is poured into it for the next layer. In this illustrative example the next pattern (e) is flat to aid in the final de-moulding and only two layers of differing $\eta$ are fabricated. The previous partially cured surface (d) essentially acts as the second layer’s pattern on the bottom to create internal MOSs. This process can be repeated for the required number of layers in which the design calls for.
Each layer can have a different $\eta$ to accurately control the flow of light through the device.

The overall fabrication time using this methodology has been reduced significantly compared to traditional soft-lithography-based approaches found in current literature. The bottleneck of PDMS-based fabrication times in literature is the degassing process used and the thermal cure time. The centrifugal casting method solves the lengthy degassing time and is detailed in Section 3.3.2. The thermal cure times have been reduced in literature with rapid curing techniques, however these have not been tested in this research. The key techniques in this methodology are detailed next.

### 3.3.1 Closed Thin Cavity Moulding

Section 2.7.3 explained the benefits of using a closed thin mould cavity for producing optical device layers of accurate thickness. The thickness in this approach is controlled and pre-set by the wall thickness of the thin cavity. This negates the need to weigh or measure the amount of polymer required for a specific thickness. Additionally, using a closed mould allows for patterns to exist on both the mould’s top and bottom which can create MOSs on both main surfaces of a layer. Creating MOSs on the top layer instead of only the bottom layer in other techniques could open a path to creating internal MOSs with a build-by-layers approach utilizing the partial curing technique described in Section 2.7.4. These benefits made closed thin cavity moulding an ideal fabrication technique for large area illuminators and collectors designed with internal MOSs. The difficulties in using such a technique were how to insert the PDMS pre-polymer without creating new bubbles, ensuring all MOS features get filled, and how to release the mould from the cured elastomer without damaging MOSs. After multiple attempts and experiments (summarized in Appendix B) using closed thin cavities, centrifugal casting using elastomeric master patterns were the key techniques to the success of this method.

### 3.3.2 Centrifugal Casting

Section 2.7.5 explained how a bubble-free product is essential in waveguide fabrication to prevent the unintentional scattering of light. In early PDMS-based fabrication experiments, the PDMS pre-polymer was required to be fully degassed before being used. Eventually, to save time during each experiment, the PDMS was quickly degassed using a centrifuge. The vacuum chamber degassing used in the earliest experiments would take anywhere from 30 minutes to an hour to fully remove bubbles from the pre-polymer. The centrifugal technique could degas the pre-polymer in as little as 30 seconds depending on the RPM of the centrifuge and the volume being degassed. Regardless of the degassing technique used, new bubbles were being created when the PDMS was inserted or set into patterned moulds. Figure 3.7 shows how the
Figure 3.6: Cross Section of the proposed build-by-layers fabrication method. a) A thin cavity mould with an elastomeric master pattern is prepared. $\eta_1$-PDMS is poured into the loading chamber and the mould assembly is attached to a spindle. b) The spindle is ramped up to several RPMs to spin the mould assembly. Centrifugal force pulls the PDMS into the thin mould cavity, filling features. Any bubbles initially present or created get diffused and pushed towards the axis of rotation. c) The loading chamber is closed off and the mould is heated for a partial thermal cure of the current PDMS layer. d) Mould is removed from heat and the top is removed. The elastomeric master pattern is carefully peeled away from the partially cured surface. e) Additional wall thickness is added and then a new elastomeric master pattern and the mould top are added. $\eta_2$-PDMS is poured into the re-opened loading chamber for the next layer and the process is repeated for the required number of layers.
PDMS would often lap over itself and fail to initially fill the small MOS cavity features which would create new bubbles. Additionally, removing air from a closed cavity with a vacuum to pull PDMS into the space instead of injecting would also often create small bubbles, only less. Sometimes, bubbles would be almost invisible to the naked eye, but when heat was applied for a thermal cure, they would expand and become very visible in the final, solidified product.

![Degassed syringe with minimal bubbles (Left). Bubbles formed from PDMS initially failing to fill 1 mm radius lens MOS cavities (Right).](image)

Figure 3.7: Degassed syringe with minimal bubbles (Left). Bubbles formed from PDMS initially failing to fill 1 mm radius lens MOS cavities (Right).

Using centrifugal force to quickly degas the pre-polymer worked so well that an idea occurred to also utilize it to fill thin mould cavities with small MOS features while simultaneously degassing the inserted pre-polymer. Figure 3.8 shows the quick proof of concept experiment which lead to the usage of this technique. A thin, 400 µm mould cavity with generic 1 mm radius lens MOS features and a PDMS loading chamber was quickly designed and fabricated. The assembly was attached to a cordless drill with a counterweight. Before spinning, it was observed that the PDMS in the loading chamber was already slowly filling the thin cavity and creating new bubbles upon interaction with the MOS features. After spinning at 1500 RPM for just 5 minutes the thin cavity and MOS features became filled with no visual bubbles present. The success of this experiment lead into the work by Mazzeo and Hardt [70]. They use this centrifugal casting method to fill microfluidic mould cavities with small channel features on both the top and bottom surfaces. Furthermore, Mazzeo [92] performed an experiment to see how thin of a mould cavity was possible using this method. He was successfully able to fill and thermally cure a 50 µm cavity section without any bubbles present, but explained how
removing it from the mould was very difficult due to how fragile the thin result was.

Figure 3.8: Centrifugal casting proof of concept experiment. Simple patterned 400 μm thin mould attached to a cordless drill with a counter weight (Left). Before spinning, the PDMS has difficulty filling the thin cavity and forms bubbles (Middle). After spinning at 1500 RPM for 5 minutes the cavity is filled and visible bubbles are gone (Right).

Mazzeo et al. [101] also performed an in-depth study on the spin rate and time required for bubbles to fully dissolve or escape the mould cavity. Spinning a mould cavity at some RPM for a length of time shorter than required will make it appear that all the bubbles have escaped, such as in Figure 3.8 on the right. However, some bubbles have actually become so small that they cannot be seen with visible light. They will then slowly accumulate with adjacent bubbles to form visible bubbles over time which will affect the final product. Therefore, it is necessary to utilize the bubble removal study results presented by Mazzeo et al. [101] to guarantee the complete removal of bubbles when using this technique. The required spin time is based on the spin rate and the closest distance from the axis of rotation in which a bubble can exist. The spin times used in Chapter 4 have been extracted from this work.

This centrifugal casting technique is the connecting puzzle piece for the illuminator and collector fabrication methodology. It allows thin cavity moulds with small patterned features on both surfaces to be used which has the potential to create internal MOSs. Additionally, the technique is capable of filling very thin mould cavities with arrays of MOSs while also
 simultaneously degassing the pre-polymer. The pre-polymer no longer needs to be degassed
prior to moulding, thus reducing the overall fabrication time. Combined with other techniques
to perform a layer-by-layer building process it presents a methodology for rapidly producing
thin, complex PDMS optical devices with industry potential.

3.3.3 Partial Curing Technique

Section 2.7.4 detailed the techniques used in literature to bond and align multiple PDMS layers.
The partial curing technique works by only curing the PDMS until slightly after solidification.
After this point, polymer chains which have not been cross-linked yet will exist on the surface.
The amount of additional curing after this point will reduce the number of uncross-linked
polymer chains and reduce the bond strength between layers. Afterwards, more uncured PDMS
is poured on top of this newly created partially cured surface where the final cross-linking of
polymer chains occurs at the interface during the next partial cure to seamlessly bond the
layers. Eddings et al. [94] found that partial curing had the highest bond strength compared
to all other bonding techniques which is essential for a robust device. Additionally, partially
cured surfaces with a MOS pattern present are able to act as the master patterns for subsequent
layers. This allows for the creation of internal MOSs by using a different \( \eta \) of PDMS for each
of the two layers. By using a partially cured surface as a master pattern it negates the need
for aligning the MOSs during the bonding process which can become a very time consuming
and complex step. Instead, master patterns are pre-aligned in the same planar location within
the mould cavity by keeping a consistent patterning area between all master patterns used.
Partial curing is the perfect technique to create internal MOSs, reduce fabrication times, and
simplify the alignment process. The challenge with partial curing is in the de-moulding step
between layers. Since the patterned partially cured surface has not undergone a full thermal
cure it is much softer and more fragile to work with. Damage during the de-moulding step
can compromise the entire device. Therefore, other techniques that reduce the possibility of
damage from de-moulding have been used in conjunction with partial curing and are detailed
next.

De-moulding a Partially Cured Surface

Section 2.7.5 described the importance of proper de-moulding to prevent damage to replicated
MOSs. This becomes even more important when de-moulding from a partially cured surface.
A partially cured surface is much softer and thus more fragile when removing a master pattern.
Therefore it was found that a release agent with a careful peeling of an elastomeric master pat-
tern greatly reduced the strain during de-moulding. Ideally, a silane-based release agent would
present the best results, as shown by the literature. However, to reduce costs, hazard, complexity, and to save time a detergent-based release agent consisting of 70% ethanol, 25% water, and 5% Dawn Ultra® detergent by volume was found to work as an effective release agent. This type of release agent works thanks to the hydrophobic and hydrophilic ends of the detergent molecules. In addition to a release agent, using an elastomeric master pattern was also found to aid de-moulding by carefully peeling it away from the partially cured surface. These two simple, yet effective techniques displayed no visible damage to MOSs during experimentation, however further research is required to evaluate the results at smaller scales.

The elastomeric pattern material used has been PDMS due to its availability and vast documentation. To apply the detergent-based release agent, the PDMS master pattern is subjected to a corona discharge for a minute to increase the pattern’s surface energy. The pattern is then dipped in the release agent and removed to rest for a short while. As the ethanol evaporates detergent molecules are attracted to the high surface energy of the PDMS. After sufficient evaporation, the pattern is carefully rinsed with deionized water to flush away any build up of detergent molecules not directly touching the PDMS surface. The steps after the corona treatment may be repeated any number of times to ensure a uniform coating of detergent molecules. Afterwards, the pattern is gently dried with an air hose and sealed in a clean container to prevent the accumulation of dust.

Elastomeric master patterns can be fabricated using the centrifugal casting technique for a single layer upon a PMMA master. Patterns can also be fabricated using the traditional PDMS soft-lithography approach with a vacuum chamber and an open mould cavity, where the thickness of the pattern is controlled by the amount of PDMS pre-polymer poured into the open cavity. The traditional approach is easier to fabricate and since PDMS master patterns may be reused many times, using this approach does not hinder the overall fabrication time. An extra bonus was also discovered when using PDMS elastomeric master patterns. The pattern was able to act as a gasket for additional sealing within the mould cavity. The outer perimeter of an elastomeric master pattern can be sandwiched in place to also act as a gasket to prevent the PDMS pre-polymer from leaking. The affect upon MOSs from slightly compressing the outskirts of master patterns still needs to be experimented and quantified, however in this research a dead-zone was used to prevent these affects. No negative affects were visible and the amount of compression induced was also added to the thickness of each layer to compensate.

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5 One to three times has worked depending on the size of MOSs
3.4 Potential Limitations of the Proposed Fabrication Methodology

There are a large number of unknowns that always exist when creating a new fabrication methodology. These unknowns can only be discovered and quantified through vast experimentation and research. With such a large and diverse project for a M.E.Sc thesis, there simply is not enough time and resources available to experiment and quantify every possible aspect of the methodology. However, through further research and the experience gained from the proof of concept experiments, some potential limitations of the methodology can be defined. The following limitations may not necessarily be true limitations, as each may have a solution that is only discoverable through further experimentation and research. Therefore, ideas for solutions are provided for each potential limitation as insight towards further experimentation.

3.4.1 MOS Replication on Partially Cured Surfaces

Section 2.7.2 described pattern fabrication techniques for large areas where the geometry of MOSs are limited by the process used. Assuming the process used is capable of creating the required MOS geometries, soft-lithography has minimal limitations pertaining to the MOS geometries replicated. Since soft-lithography can replicate any surface imperfections [56], the limitations actually occur during the pattern de-moulding process. For example, Figure 3.9 illustrates complex PDMS MOS geometries which would be very difficult to de-mould without damage, even when using an elastomeric master pattern with release agent. Since the base diameter is much smaller than the height or upper width, these MOSs are likely to break at the base. When de-moulding a master pattern from a partially cured surface, this limitation worsens. In this case, the base diameter may break at larger relative radii. The upside-down half-cones produced by Lee et al. [11] may prove very difficult using this technique, thus further experimentation is necessary before proceeding with such a design.

When the MOS-filled partially cured layer is to act as the subsequent master pattern in this methodology, another potential limitation occurs. It is unknown the effect of large centrifugal forces upon soft MOSs and if permanent deformation will occur. These large forces will occur when increasing the spin rate of the moulds in order to reduce fabrication time. This is more likely to occur on high aspect ratio MOSs where bending away from the axis of rotation is a concern. Further research and experimentation is required to see the affect of such forces upon soft MOSs. As starters it would be beneficial to measure the mechanical material properties of partially cured PDMS and use finite element software to simulate these forces upon different geometries of MOSs. The work done by Mazzeo et al. [101] shows that lower spin rates can
be used in this methodology, but will add considerable fabrication time due to centrifugally casting multiple layers. To avoid this possibility in proof of concept experiments, only spin rates less than 4000 RPM were used. It is possible that the aspect ratio of MOSs is related to the maximum spin rate which can be used for a partially cured master pattern. With this information, the spin rates and spin times can be optimized for different illuminator and collector designs.

Another potential issue may occur when the viscous PDMS pre-polymer is pulled into the mould cavity from the loading chamber using centrifugal force. This rapid, yet viscous flow passing over MOSs present on a partially cured layer may also cause permanent damage. Again, finite element flow simulations on a MOS patterned surface will reveal if this affects them. To account for this possibility in the proof of concept experiments presented in Chapter 4, the spin rate was slowly increased to allow the pre-polymer more time to fill the cavity, however it is unknown if this was necessary due to the geometries of MOSs created.

3.4.2 Centrifugally Casting a Large Area

The proposed fabrication methodology is capable of creating illuminators and collectors with a relatively large area. However, when this area increases beyond 1x1m the centrifugal force present in a mould at the furthest location from the axis of rotation becomes extremely high. Since centrifugal force has been defined in this research as the reaction force to centripetal force, the magnitude of both with an object of mass $m$ moving at angular velocity $\omega$ along a path with radius of curvature $r$ is given by the following well-known equation for centripetal force:

$$F = mr\omega^2$$  \hspace{1cm} (3.1)
Eq. 3.1 shows that as \( r \) increases, or the length of illuminators and collectors from the axis of rotation increases, the magnitude of centrifugal force also increases. Additionally, as \( r \) increases, it is expected that \( m \) will also need to increase using the same mould materials, adding even more to the overall magnitude. This directly translates to an increase in overall forces upon a mould system as the required area of illuminators and collectors increases. Rotating the mould at a higher angular velocity, \( \omega \), will also greatly increase the centrifugal forces due to the exponent in Eq. 3.1, therefore if a larger area is required the spin rates may be reduced to account for the increase in centrifugal forces from a larger \( r \) and \( m \). Unfortunately, a reduction in \( \omega \) will increase fabrication times. In theory, a large system with strong materials can be designed to withstand these forces, however the cost to design such a system may not be feasible and ultimately there will be a limit on the total area where such a fabrication methodology is impossible even with the strongest materials.

### 3.4.3 Carefully Peeling a Large Area

Section 3.4.1 above explained how certain MOS geometries may be near impossible to de-mould from a partially cured surface; even using the careful peeling technique. The careful peeling technique is slightly "feel-dependent", meaning that the user performing the technique can feel and predict when a specific area of a MOS pattern may have additional difficulty in de-moulding, potentially causing damage. The user can then modify their approach and attack from a different peeling angle to prevent it. An automated process with accurate sensors may help, however as the area to de-mould increases this may become increasingly difficult to detect. The MOS geometries and release agent used will directly affect the outcome where additional experiments performed on much larger areas of MOSs will be required to optimize the process for scalability. Master patterns which have zero adhesion to a partially cured layer would be ideal.

### 3.4.4 Curing PDMS - Shrinkage Affects

Section 2.7.1 explained how PDMS shrinks when curing at higher temperatures during the soft-lithography process. The Section also described a gel point where after which shrinkage affects no longer occur. This is the point in the curing process where the PDMS pre-polymer has solidified and temperature dependent shrinkage occurs at this point. In the proposed fabrication methodology, a layer is partially cured, essentially just past the gel point, and then a new uncured layer is applied on top of it. It is unknown if the potential shrinkage of this new layer will affect the already solidified and partially cured layer before it becomes completely cured. Additional experiments are required to see this potential affect. A partially cured layer’s
MOSs must be measured before additional curing occurs, and then once the subsequent layer is applied and cured, the internal MOSs must be measured for a comparison.

To achieve truly fast fabrication times, high curing temperatures must be used where the shrinkage of PDMS is unavoidable. However, there may exist additional techniques to account for the induced shrinkage. Since the shrinkage ratios for PDMS at multiple temperatures have been documented [84], potential mould features can be added to absorb the affect, preventing the unintended effects to replicated MOSs. One such example is to slowly reduce the mould cavity’s total volume during the curing process. Since the shrinkage ratios are anywhere from 0.1 – 5% depending on temperature, the reduction in cavity volume from reducing the thickness and length/width would be small. This could be achieved with added materials where the expansion or contraction can be controlled. The piezoelectric effect or a combination of materials which thermally expand at a similar shrinkage rate could be utilized. This approach will likely require some calibration of MOS geometries where they must be designed larger to account for these shrinkage affects; assuming the above experiment suggestions show shrinkage of MOSs on partially cured master patterns.

### 3.4.5 Centrifugal Affect on PDMS-TiO$_2$ Composites

Centrifugation is a process used in industry and laboratories to separate heterogeneous mixtures. It uses centrifugal force to remove aggregates from a mixture. When TiO$_2$ nano-particles exist in the PDMS pre-polymer, there may be an unintended affect upon these particles during the centrifugal casting stage. Depending on the type of mixture required for the TiO$_2$ nano-particles to increase the $\eta$ of cured PDMS, the centrifugal force may disperse these particles non-uniformly, thus increasing the $\eta$ in a non-uniform fashion. This could be observed with a few simple experiments where the PDMS-TiO$_2$ composite pre-polymer is centrifugally cast and $\eta$ measurements are taken along an axis normal to the axis of rotation. On a different note, if the PDMS-TiO$_2$ pre-polymer is a solution, then the centrifugal casting stage may help the dispersion of nano-particles and actually remove any missed aggregates in the original composite pre-polymer mixing stage. These potential aggregates could then be allowed to exist in a sacrificial area, furthest from the axis of rotation in the mould’s layer and then removed later.

### 3.5 Contribution to Science & Technology Discussion

To reiterate, large area flexible illuminating or collecting waveguides fabricated with PDMS do not exist in current literature. Furthermore, internal MOSs to create a robust product are also new to science. The presented fabrication methodology in this Chapter brings these aspects to
life. By utilizing centrifugal casting and a careful peeling of a partially cured surface, infinite layers in a bottom-up fashion can be accomplished where MOSs exist between each layer. With further research and experimentation this fabrication methodology is capable of creating very complex multi-layered flexible optical devices in a timely manner.

Previously, fabrication with PDMS has been considered very time consuming due to lengthy bubble removal, layer alignment and thermal cure times. This methodology has the potential to solve these issues. The centrifugal casting negates the need to remove bubbles from the mixed pre-polymer prior to casting. It also aids in filling small MOSs within the thin cavity, however further experimentation is required to find how small of MOSs are possible with different spin rates. The careful peeling of an elastomeric master from a partially cured surface also negates the need to carefully align and bond patterned layers. Instead, master patterns are pre-aligned within the mould cavity prior to curing where casting directly upon a partially cured layer bonds the subsequent layer. The combination of these existing techniques to efficiently fabricate illuminators and collectors is a new contribution to science and technology.

3.6 Concluding Remarks

This chapter has presented a fabrication methodology for large area illuminators and collectors which has the capability of creating internal MOSs in a timely manner. The methodology uses a combination of existing techniques found in microfluidics literature. Centrifugal casting, partial curing, and soft-lithography are the major components to the methodology. This chapter has also attempted to show and touch on some of the many unknowns which still exist using this methodology. Through further experimentation and optimization this fabrication methodology has the potential to be used in industry for a variety of multi-layered PDMS optical devices with internal MOSs.

The next chapter presents a proof of concept experiment using this fabrication methodology to create a working 3-layer illuminator with an embedded LED. Proof of three bonded layers and internal MOSs existing between the top core and cladding layers is visualized through functionality images and microscope captures to prove the feasibility of this methodology.
Chapter 4

Feasibility Study - Fabrication of Functional Prototypes

4.1 Introduction

To demonstrate the feasibility of the methodology presented in Chapter 3 two main sets of fabrication-based experiments were performed and qualitatively examined. Prior to these main experiments, many other ideas, moulds, and techniques were tested which ultimately formed into the current methodology. These experiments are summarized in Appendix B where the vast challenges in developing a practical fabrication methodology for illuminators and collectors are summarized.

The first experiment presented in Section 4.2 demonstrates the fabrication methodology and its ability to create almost any illuminator or collector design. A two-layer design where the top layer is a collector and the bottom layer essentially acts as an illuminator is fabricated using the methodology. The prototype’s fabrication had minor difficulties while carefully peeling the top master micro-optical structure (MOS) pattern from the partially cured first layer. Lessons from this experiment were later transferred into the final experiment presented in Section 4.3 where a three-layer illuminator with internal MOSs is fabricated. This final experiment used moulds with a much larger area than any previous experiment. The resultant prototype illuminators proved the feasibility of the fabrication methodology, especially the use of centrifugal casting to form bubble-free thin layers. The prototypes proved to have a strong three-layer bond with MOSs present between the core and top cladding layers. It was difficult to see the internal MOSs when using the non-ideal base-to-agent ratio technique for modifying the $\eta$ of polydimethylsiloxane (PDMS). Therefore, two additional prototypes were fabricated using food colouring in the middle core layer to clearly show the existence of three layers and internal
MOSs.

The fabricated prototypes from both experiments were not measured for their efficiency or functionality as they were never expected to perform well due to the lack of essential design aspects described in Section 3.2. Instead, images of the prototypes were taken to convey some minor functionality and prove there exists multiple layers with MOSs embedded in between cladding and core layers. By proving the existence of internal MOSs and multiple bonded PDMS layers, the feasibility of the fabrication methodology has been demonstrated.

### 4.2 Fabrication of a Collector and Illuminator Combined Prototype

To verify the plausibility of this fabrication method, a prototype involving a combination of collecting and illuminating MOSs was first fabricated [108]. The design was based off Zemax OpticStudio simulations where micro-lenses concentrated light onto wedge features which redirected the light towards an area with diffusing MOSs. Figure 4.1 on the left shows the computer-aided design (CAD) model of the prototype which has a concentrator region as well as a diffuser region. The incident light upon the concentrator region is focused by an array of micro-lenses onto an array of micro-wedges which redirects the light within a layer of higher $\eta$ towards the diffuser region. The diffuser region consists of long wedge features which reflect the light back out of the prototype opposite of the original incident direction. Figure 4.1 on the right illustrates the MOSs which produce this combined effect. The design utilizes two PDMS layers where the top layer has a lower $\eta$ and the bottom layer has a higher $\eta$ for guiding light through total internal reflection (TIR).

![Figure 4.1: CAD model of the combined prototype (left). Illustration of collecting and illuminating MOSs working together: micro-lenses concentrate light onto wedge features which redirects the light towards an area with diffusing MOSs (right).](image-url)
This design is not one that could be considered robust as described in previous Chapters. There are no internal MOSs and TIR is functional due to the low $\eta$ of air. However, a two-layer device was fabricated using this methodology and exhibited some functionality. Figure 4.2 shows how the original poly(methyl methacrylate) (PMMA) MOS patterns were fabricated. A computerized numerical control (CNC) machine using micro-tools with a polished surface was used to give an optical surface finish for MOSs on soft plastics. The wedge PMMA master (right) was later inversely replicated onto PDMS to act as one of the two key master patterns. These two key master patterns were used for the top and bottom surface MOS arrays (Figure 4.1) while a simple flat PDMS master was used between these layers for the partial curing and careful peeling techniques.

Figure 4.2: Lens pattern fabricated with an optical quality ball-nose end mill (left). Wedge and diffusing pattern fabricated with an optical quality flat end mill and an angled set-up (right).

Figure 4.3 shows the very basic centrifugal moulding system using a common drill press. The bottom layer was first centrifugally cast using a 5:1 base-to-agent mixing ratio ($\eta \approx 1.424 @460$ nm). For both layers, the mould was spun at 2400 RPM for 8 minutes based on the work by Mazzeo et al. [101]. The 8 minutes used at this spin rate is slightly more than required for 100% bubble removal. This was simply to ensure that all bubbles are removed, since after curing there are no second chances if a bubble still exists. After spinning, this layer was partially cured for 24 hours\textsuperscript{1} at room temperature to avoid both PDMS shrinkage and the large thermal expansion effects of heating a PMMA mould (see Table 2.5). Once partially cured, the top of the mould was removed and a flat PDMS pattern was carefully peeled from the partially cured surface in preparation for the next layer. The final top layer was centrifugally cast over the previous partially cured layer using a 20:1 base-to-agent mixing ratio ($\eta \approx 1.417 @460$ nm). After using the same spin rate and time, the mould was left to fully cure over 72 hours\textsuperscript{2}.

Figure 4.4 shows the resultant collector-illuminator prototype. A minor de-moulding issue occurred while carefully peeling the flat PDMS pattern used between the two layers. The ini-

\textsuperscript{1} 50% the total cure time with a 5:1 ratio supplies a solid, yet somewhat sticky partially cured surface.

\textsuperscript{2} Less curing agent due to a 20:1 ratio takes longer to fully cure.
Figure 4.3: Two PMMA moulds are attached to a drill press for fabrication of a two-layer combined prototype.

Partial peeling from the diffuser end of the prototype began to lift off the bottom pattern. Once this lifting occurred, a new attack angle for the careful peeling technique was chosen from the opposite end of the prototype. This attempt did not lift from the bottom pattern and continued through until reaching the previous damage where some tearing of the layer occurred. This lifting issue was later solved in Section 4.3.3 by adding a sacrificial zone around the patterned region of interest and introducing a small trench intended to hold the partially cured PDMS upon the bottom surface of the mould. The prototype was placed in a partitioned light box that only allowed the collector region to receive light from an external source. The collector region focused light onto the small wedges and directed it towards the illuminator region where light was directed back towards the source’s general direction. The result demonstrated the plausibility of both the collector-illuminator concept as well as the proposed fabrication methodology.

During the centrifugal casting process for this experiment PDMS leaked out of the PMMA mould due to the large pressures induced when spinning at 2400 RPM. The PMMA mould did not allow for enough clamping force using screws without cracking the material. Additionally, from prior experience heating such a mould was avoided due to PMMA’s large thermal expansion coefficient which combined with PDMS’s shrinkage would cause warping and damage to a layer. Therefore, a mould material upgrade was required for the next and final experiment series.
4.3 Fabrication of a 3-Layer Illuminator

To truly demonstrate the feasibility of the fabrication methodology described in Chapter 3 several three-layer illuminator prototypes were fabricated. The centrifugal moulding system, detailed in the next section, used two moulds for balance to create two prototypes per experiment. The prototypes were designed with an area of $160 \times 60$ mm while the mould cavity itself had an area of $190 \times 90$ mm. This new area is approximately double the area of all previous experimental prototypes. During the initial fabrication trials, unforeseen difficulties arose due to the larger moulding area. These issues were solved for later trials where the quality of prototypes produced increased. This Section covers the fabrication system and equipment used, the general fabrication procedure followed, each trial of prototypes fabricated, and discusses the proof of feasibility of the proposed fabrication methodology.

A 3-layer illuminator was the prototype flexible optical device of choice due to simplicity in functionality and design. An efficient collector requires that the redirecting MOSs below the lens MOSs be very small relative to the lens diameter so that propagating light waves headed
toward the detector or photovoltaic cells will be less likely to interact with adjacent redirecting MOSs. This type of design is present within the collector and illuminator combined prototype which uses air as the cladding ($\eta_{\text{air}} \approx 1$) in Section 4.2 above. However, when designing for internal MOSs using the base-to-agent ratio technique, Eq. 2.7 with $\Delta \eta = 0.007$ equates to a critical angle, $\theta_{\text{crit}}$, of approximately $84^\circ$ which thus requires very steep redirecting MOSs in collectors. These steep and small MOSs are very difficult to create using a traditional CNC machine, making visually functional collectors difficult to fabricate. Illuminators with $\theta_{\text{crit}} \approx 84^\circ$ on the other hand, require very shallow redirecting MOSs which can be much larger and still visually display some functionality. Therefore, the master patterns for an illuminator are considered much easier to fabricate for demonstrating the fabrication methodology. Two master patterns were fabricated to create two different illuminator designs. The next Section details the master pattern designs where one uses long wedges to redirect light out of the core layer and the other uses small domes to diffuse light from the core in multiple directions.

4.3.1 Fabrication System and Equipment

Centrifugal System

A custom aluminium centrifugal casting mould was designed, fabricated and tested multiple times to prove the feasibility of the fabrication methodology described in Chapter 3 (See Appendix C for details on CAD drawings and components). Figure 4.5 shows the centrifugal moulding system set-up for its first trial. The system consists of a propeller and drive shaft mounted in a CNC machine’s spindle to accurately spin the moulds and supply safety via the machine’s encasing. A block with a bearing is present at the base within a vice to absorb any potential non-axial loading. Bolted to the propeller are two thin cavity moulds which balance the system. The system has been designed to spin at 1000 RPM when fully loaded which gives a factor of safety of approximately 3.26 (see Appendix D for full finite element analysis).

Unlike Figure 3.6 where the PDMS is directly pulled into the thin mould cavity via a loading chamber, this design uses a simple side by side inlet and outlet for injecting PDMS with a syringe. Figure 4.6 illustrates using CAD how the inlet and outlet forms a seal against the master patterns. A flange is pulled up against the elastomeric master pattern which essentially acts as a gasket to prevent the PDMS from escaping. This technique simplifies the design and fabrication of the moulds, however it adds a considerable amount of time to the overall fabrication length. Using a simple inlet requires multiple filling and spinning to completely fill the thin cavity with PDMS. The strategy is to inject PDMS until it begins to escape from the outlet and then spin the moulds for several seconds to force the newly injected PDMS to the furthest

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3 Multipurpose 6061 aluminium was purchased and used from McMaster-Carr®
Figure 4.5: Two centrifugal moulds mounted within a CNC machine spindle. The mould assembly is spun at 1000 RPM for over 17 minutes to remove all bubbles from each layer and fill MOS cavities.

point within the cavity from the axis of rotation. This is repeated a few times until injecting new PDMS instantly causes PDMS to escape from the outlet, indicating the cavity has been filled.

3-Layer Moulds

Each mould consists of 6 pieces which are all bolted into the base propeller. Figure 4.7 illustrates each piece of the mould. Two elastomeric (PDMS) master patterns are placed within the pattern holder mould pieces which also pre-align the MOSs. When fabricating the first layer for a 3-layer illuminator only 4 of the 6 mould pieces are used where the cladding spacer sets the first layer’s thickness. For the second layer, the core spacer is added to set the new thickness and then finally the second cladding spacer is added for the thickness of the third and final layer.

Thirty-two screws hold each mould assembly together and fix it to the propeller as seen in Figure 4.5. Two 0.25” steel dowel pins are also present in each mould assembly for alignment purposes. The total sixty-four screws are each torqued to 22 in-lbs which is near the maximum recommended value for 10-32 screws in 0.25” threaded 6061 aluminium. The large number of screws spaced 20 mm apart ensure that no PDMS will escape from the system during the 1000 RPM spin. When the centrifugal system is in operation, the centrifugal force induces a higher
Figure 4.6: Cross-section CAD illustration of the sealed inlet and outlet design using a flange for inserting PDMS into the thin mould cavities. Common zip-ties were used on the clear tubing to hold the flange against the elastomeric master pattern.

Figure 4.7: CAD illustration of the mould’s pieces to create 3-layer illuminating prototypes. The first layer uses the cladding spacer to set its thickness while the second layer will require the core spacer. Finally, a second cladding spacer is added for the third layer.

pressure upon the pre-polymer which in previous PMMA-based experiments caused minor leaking of PDMS. More screws than necessary were added to prevent this from happening, even at higher spin rates.

**Master Patterns**

Two different illuminating PDMS master patterns were fabricated for the two-mould balanced system. The original master-master patterns were fabricated on PMMA using a traditional CNC machine with the same optical quality tools mentioned in Section 4.2. Figure 4.8 illustrates the CAD used to fabricate the PMMA master-master patterns. The wedge pattern on the left was fabricated with the stock PMMA angled 5° to the horizontal using a 1 mm diameter flat end-mill with the same milling technique previously illustrated in Figure 3.4 and described in Section 3.2.2. The wedges linearly increase in height along the length of the pattern to supply
the uniform illumination described in Section 2.4.5 and previously illustrated in Figure 2.10 on the left. The dome pattern on the right was fabricated using a 2 mm diameter ball endmill treated as a drill. The depth of the inverted domes are increased along the length of the pattern which ultimately increases their size to supply uniformity as previously illustrated in Figure 2.10 on the right.

Figure 4.8: CAD illustration of the two illuminating negative master patterns. These patterns were fabricated on PMMA and later inversely replicated onto PDMS.

Table 4.1 summarizes the geometrical parameters of the MOSs in each master-master pattern. Available tools determined the sizes of the MOSs while spacing and heights were chosen arbitrarily. A brief simulation was performed in Zemax OpticStudio which showed that the $\Delta \eta = 0.007$ supplied an efficiency of roughly 8% and 25% light diffusing out of the illuminating surface for the wedge and dome patterns, respectively. As Section 3.2 explains, an ideal and fully functional illuminating prototype is not required to prove the feasibility of the fabrication method, therefore these inefficient MOS patterns with larger, arbitrary parameters are deemed adequate.

Table 4.1: Geometrical parameters of illuminating dome and wedge pattern MOSs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Domes</th>
<th>Wedges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of MOSs</td>
<td>1863</td>
<td>172</td>
</tr>
<tr>
<td>Diameter/Width</td>
<td>0.87-2 mm</td>
<td>0.9 mm</td>
</tr>
<tr>
<td>Height</td>
<td>0.1-1.35 mm</td>
<td>0.1-1.35 mm</td>
</tr>
<tr>
<td>Centre-to-centre spacing</td>
<td>2.25 mm</td>
<td>0.9 mm</td>
</tr>
<tr>
<td>Angle</td>
<td>N/A</td>
<td>5°</td>
</tr>
</tbody>
</table>

The PDMS master patterns were fabricated by casting PDMS pre-polymer over the PMMA
masters. A simple PMMA mould with a 4.2mm thick cavity was used to create the 4.2mm thick PDMS master patterns. Since the mould is required to make a single and relatively thick layer of PDMS, one end of the mould was left open and 5:1 base-to-agent ratio degassed PDMS was carefully poured in. The mould was oriented vertically and left to fully cure over 48 hours at room temperature. A room temperature cure allows any bubbles created during the casting time to escape the main area of the cavity. A sacrificial zone existed at the top of the vertical cavity where bubbles will fail to pop from surface tension. This zone was later cut away when PDMS master patterns were removed from the moulds.

Figure 4.9: Resultant wedge (left) and dome (right) PDMS master patterns after casting over fabricated PMMA patterns.

Figure 4.9 shows the resultant PDMS master patterns which are used for the fabrication of the second layer for the 3-layer illuminating prototypes. These two patterns will be fixed in the top pattern holder mould piece illustrated in Figure 4.7; thus there exists inlet and outlet
recesses to fit the flange described above. Outside the patterned area exists a sacrificial area which will absorb any potential air bubbles leaking in during the thermal cure and for preventing de-moulding damage on the patterned area. Two additional flat-surface PDMS patterns were also fabricated to replicate smooth surfaces for the bottom surface, bottom cladding-to-core interface, and top surface of the prototypes. They have been fabricated out of an elastomeric material (PDMS) for the careful peeling technique. Figure 4.10 shows the flat-surface PDMS master patterns used in the fabrication of the 3-layer illuminating prototypes. The left flat-surface pattern is used for the cladding-to-core interface for the first layer’s fabrication as well as the prototype’s top surface for the third layer’s fabrication. This pattern will be fixed in the same pattern holder as the dome and wedge patterns for fabricating layers 1 and 3. The right flat-surface pattern is used for the bottom surface of the prototypes and will be present for all 3 fabricated layers. This pattern will be fixed within the bottom pattern holder mould piece illustrated in Figure 4.7. A small, thin trench was cut with a knife into the sacrificial area to aid in holding cured PDMS upon this pattern’s surface during the careful peeling processes of each layer.

4.3.2 Fabrication Procedure

To create sets of illuminating prototypes, a general fabrication procedure was followed. However, due to experimenting with a new mould material and size, a few miscellaneous aspects of the procedure were optimized and altered in later trials. Figure 4.11 illustrates via flow chart the critical fabrication steps to create one of the three layers. These steps follow the methodology described in Section 3.3 to fill, degas, cure, and carefully peel each layer.

Set-up and assembly took a considerable amount of time and patience. Before each trial experiment, the PDMS master patterns were fully cleaned and a detergent-based release agent was applied. Section 3.3.3 described the detergent-based release agent which consisted of 70% ethanol, 25% water, and 5% Dawn Ultra detergent by volume. Since this release agent is essentially a cleaning surfactant, it was also used to remove any dust or small bits of cured PDMS which became attracted to the pattern after each trial. To apply the release agent a corona discharge was applied to a master’s patterned surface to first increase its surface energy (Figure 4.12). The detergent-based release agent was then poured over the patterned surface, covering the entire area. Approximately a minute was given for the detergent molecules to settle and become attracted to the charged surface. The surface was then carefully rinsed with deionized water and then gently dried for several minutes with an air gun. Patterns were then placed in sealed containers to protect them from attracting dust.

Once the master patterns were ready, the fabrication procedure could begin. The centrifugal
Figure 4.10: Flat-surface PDMS patterns used for the fabrication of 3-layer illuminating prototypes. The pattern on the left is used for the cladding-to-core interface for the first layer’s fabrication as well as the prototype’s top surface for the third layer’s fabrication. The pattern on the right is used for the bottom surface of the prototypes and will be present for all 3 fabricated layers. A small, thin trench was cut within the sacrificial area to hold PDMS upon this pattern during the careful peeling processes.

mould system is then assembled for the first layer. The alignment pins are inserted into the propeller base and the bottom pattern holder is added. The flat pattern with a trench shown in Figure 4.10 on the right is inserted into the bottom pattern holder. The three other mould pieces and top pattern are assembled separately before being added to the full system. The mould top and top pattern holder are assembled first with another set of alignment pins. The top flat pattern shown in Figure 4.10 on the left is inserted into the top pattern holder, against the top surface of the mould top. A cladding spacer is added to hold the pattern in place. The cladding spacer controls the thickness of this first layer. Since the spacer is 1.27 mm thick and both the top and bottom master patterns are compressed by 0.2 mm to form a seal, this first cladding layer is 0.87 mm thick. Tubes with flange couplers are inserted through each
Figure 4.11: Critical procedure steps for the fabrication of a single layer with the centrifugal mould assembly.

inlet/outlet location as illustrated in Figure 4.6 where zip ties are then added to the other side to keep them in place and pressed up against the elastomeric master. This new sub-assembly is then inverted and added to the previously assembled base. The alignment pins are pushed out via the base’s alignment pins to keep the assembly together when adding the sub-assembly. After assembly, 32 screws are added to each mould assembly and torqued to 22 in-lbs. The resultant assembled system is now as illustrated in Figure 4.5.

Once assembled, the system is placed within the CNC machine’s spindle and lowered into the bearing block. For the cladding layers, 20:1 base-to-agent ratio PDMS pre-polymer is injected into each mould assembly until the liquid begins to escape from the outlet. The spindle is then turned on and slowly increased to 800 RPM for approximately 30 seconds. This quick spin forces the injected PDMS to the furthest location from the axis of rotation (and inlet/outlets) to create new space to add additional PDMS pre-polymer. More PDMS is added to the mould and this process is repeated until adding additional PDMS instantly causes PDMS to escape from the outlet, at which point the mould cavity is considered full. Once full, the spindle is turned on and slowly ramped up to 1000 RPM and remains at this spin rate for 20 minutes. The time required for 100% of bubbles to escape or dissolve inside the cavity is extracted from the work done by Mazzeo et al. [101] where it takes approximately 17 minutes to completely remove a critical diameter of bubbles at 1000 RPM. The additional spin time is simply a precaution since
the data is based off the viscosity of 10:1 PDMS and 20:1 PDMS is slightly more viscous.

After 20 minutes of spinning the entire mould assembly is transferred to an oven set at 65 °C (Figure 4.13) to partially cure the layer. 65 °C was the temperature used to reduce PDMS shrinkage as well as to reduce the amount of thermal expansion induced by the assembly. A full PDMS cure at this temperature takes approximately 2.5 hours. A 20:1 base-to-agent PDMS layer was found to take approximately 1.75 hours to partially cure since it has less curing agent in it. This cure time was found during previous experiments by curing PDMS in an open cavity and periodically feeling if the surface had solidified, but was still slightly sticky, meaning there still exists some uncross-linked polymer chains. After the 1.75 hours the mould assembly was removed from the oven and left to cool down for 20 minutes\(^4\). Once cooled, the alignment pins and all 64 screws were removed. The mould top and top pattern holder pieces were carefully removed and the alignment pins are re-inserted to hold the rest of the mould assemblies in place. The top pattern is then carefully peeled from the partially cured layer. Figure 4.14 shows the careful peeling step in the process where the master pattern is curled and pulled from the soft layer to prevent damage. A better release agent, such as the silane release agents described in Section 6 could ease this careful peeling process further, however the detergent release agent proved successful in prototype fabrication with a little patience.

After carefully peeling the master pattern from the partially cured layer, the mould assemblies are set-up for the next layer. The process for this layer is almost identical to the last, however for this layer the PDMS master patterns shown in Figure 4.9 are used in place of the

\(^4\) The first failed trials revealed that it takes approximately 20 minutes for the full assembly to reach 65 °C inside the oven. Therefore to cure for 1.75 hours the same amount of time was given for cooling.
previous top patterns and the core spacer is added to set the mould cavity thickness. The core spacer is 2.03 mm thick and again there exists 0.2 mm of compression for sealing against the pattern, thus thickness of the core layer is 1.83 mm. A light emitting diode (LED) strip is adhered to the partially cured layer at a location just before the MOS pattern. The moulds are then assembled, sealed, and PDMS is injected all in the same manner as the previous layer. The injected PDMS for this layer is of a 5:1 base-to-agent ratio to create a slightly higher η for the core layer. The system is then spun once again at 1000 RPM for 20 minutes and placed into a 65 °C oven. Since this core layer has more curing agent, the layer is partially cured in the oven for 1.15 hours until it is removed and cooled for 20 minutes.

After partially curing the second layer, the mould is disassembled and the careful peeling technique is applied to remove the top MOS pattern. After which, the third and final layer is prepared in an identical manner to the first. Since this third layer uses another cladding spacer which is 1.27 mm thick and compresses by 0.2 mm against the top flat pattern, the final cladding cavity is 1.07 mm thick. After injecting 20:1 PDMS and spinning a final time, the mould assembly is set in the 65 °C oven for 2.5 hours to perform a full cure of the final layer. After cooling, the prototype is removed from the mould and the sacrificial areas are cut away. The following sections detail the experiment trials and resultant prototypes which prove the feasibility of this fabrication methodology.
Figure 4.14: Carefully peeling a flat pattern from a partially cured PDMS surface. The partially cured layer is very soft, therefore the flat pattern is curled and pulled from the surface. Suction and adhesion prevents the ability to simply lift the pattern from the layer without causing irreversible damage.

4.3.3 Experiment Trials

The centrifugal mould system was designed and built based off previous PMMA mould iterations. This new mould assembly fabricates over double the area of previous moulds. This larger area led to a few unforeseen issues during the initial experiment trials which were solved by the later trials. The following Sections detail each trial from failure to success. After the first successful trials, it became clear that visibly seeing MOSs and multiple layers would be difficult due to the low $\Delta \eta = 0.007$ supplied by the base-to-agent mixing ratio $\eta$-modifying technique detailed in Section 2.6.3. Therefore, in the last two trials food colouring was added to the core layers of each prototype for clear visibly of internal MOSs and multiple PDMS layers. Since colouring was to be used instead of a $\Delta \eta$, the standard PDMS mixing ratio of 10:1 base-to-agent could also be used which actually replicates the ideal $\eta$-modifying technique using commercial nano-particles detailed in Sections 2.6.3 and 3.2.1. Using a 10:1 ratio for the first
thin cladding layer was much easier to carefully peel the PDMS master patterns from. This is because 20:1 ratio PDMS is much softer than 10:1 ratio PDMS.

![Image](image_url)

Figure 4.15: PDMS filled with many gas bubbles from mixing is injected into the centrifugal moulds. These bubbles are removed during the mould’s 1000 RPM, 20 minute spin stage.

The PDMS mixed for each trial was not degassed prior to usage. Figure 4.15 shows how bubble-ridden mixed PDMS was injected into the mould cavities. According to the research performed by Mazzeo et al. [101], a spin time of 17 minutes at 1000 RPM will completely remove all bubbles in the cavities. A considerable amount of fabrication time was saved by not having to degas PDMS prior to usage, such as the standard vacuum chamber technique often used in microfluidics fabrication which is detailed in Section 2.7.5. Another observable note which is also found in every experiment trial and likely stems from the mould thermal expansion described in Section 2.7.5 is shown in Figure 4.16. When the full mould assembly is heated for thermal curing, the expansion of the aluminium and elastomeric master patterns appears to push some of the PDMS back out of the mould. This causes the PDMS closest to axis of rotation to cure slightly less than PDMS at the opposite end. It is likely due to the slow flow of PDMS being pushed out of the mould, much like how a slow flowing stream of water has difficulty freezing in the winter. This is a fabrication issue that is currently unsolved and likely affects the intended layer thickness and quality. Section 5.3 describes the future work for this fabrication methodology where this issue could be solved by thermally curing layers while spinning at high RPMs. In an attempt to prevent damage due to this issue, the careful peeling process is always performed from the end of the mould furthest from the axis of rotation, and thus is started at the most cured location. This way, if the layer is damaged due to the less-cured PDMS near the axis of rotation the area of the layer which did not damage can be salvaged.
Once damage begins to occur it is very difficult to stop it from continuing to damage the rest of the layer, much like preventing a tear in a chip bag from becoming larger over time.

Figure 4.16: When the centrifugal mould assembly is heated, the thermal expansion of the materials push the PDMS back out of the inlet/outlet locations creating a thinner-than-intended layer with less-cured PDMS closer to the axis of rotation. This effect is worsened if air existed under the master PDMS patterns prior to thermal curing.

**Trial 1**

The first experimental trial of the centrifugal mould assembly unfortunately went poorly. The experiment did not continue past the first cladding layer. After partially curing the layer for 1.75 hours in the 65 °C oven, one of the moulds was promptly disassembled. It was discovered that the PDMS was not quite partially cured. Figure 4.17 image a) shows the result of attempting to carefully peel from an uncured layer. The master pattern had lifted easily, however since the PDMS was far softer than expected it deformed and attempted to release from the bottom master pattern, tearing in several places. The lesson learned was the mould assembly requires time for the heat to reach the PDMS inside the cavity which also means the cavity will stay warm for some time after removal from the oven. 20 minutes was found to be enough time for the mould and cavity to cool before disassembly.

The 20 minute cooling time also allows the cavity layer to continue to cure outside the oven due to the residual heat inside the cavity. Thus, after 20 minutes the second mould cavity had been correctly partially cured. Unfortunately, even with proper curing this layer broke during the careful peeling process. Figure 4.17 images b) and c) show how the layer tore closer to the

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5 Damage being tears in the partially cured layer, or the layer lifting from the bottom master pattern as opposed to the intended top pattern.
Figure 4.17: Results of a failed first experiment trial. This trial did not continue past the first cladding layer. a) Major de-moulding damage of the layer in mould #1. The layer was far softer and uncured than expected. With this insight, mould #2 was left to cool for 20 minutes. b) Mould #2’s layer greatly thinned in the middle and closer to the axis of rotation and during the careful peel it broke off from the bottom pattern. c) Peeled PDMS master pattern with broken layer adhered to it.

An axis of rotation. A closer look at these images reveals how thin the layer becomes, especially in the centre of the mould cavity. This was due to the elastomeric master patterns failing to stay flat upon the mould’s top and bottom surfaces. Gravity caused the top PDMS master pattern to essentially sag from the upper mould surface. This sagging left an air gap which eventually expanded and pushed the two master patterns closer together within the mould cavity, making the layer of PDMS extremely thin and nearly impossible to de-mould\(^6\) without causing damage.

\(^6\) Impossible to de-mould using the detergent-based release agent. Better release agents, such as silane-based agents may be capable of easily releasing from any layer thickness.
Trial 2

The master pattern sagging issue found in the first trial was solved by adding a 0.0625” thick piece of polyethylene terephthalate glycol-modified (PETG) underneath the patterns. The sheet of PETG has a smooth surface which the PDMS master patterns adheres to via van der Waals force and simple suction. To add the PETG, the moulds were modified by removing a 0.0625” deep pocket and adding the plastic sheet. This modification solved the pattern sagging issue and kept the layers a consistent thickness.

Another modification to help the careful peeling process was also added. Experience from the previous trial found it was difficult to start carefully peeling only the top master pattern from the layer and not both the pattern and layer from the bottom master pattern. Once peeling started from either of these master patterns, it was simple to continue, but not to change which surface the layer was peeling from. Therefore, additional release agent was wiped onto the sacrificial area of the top patterns. This release agent was left to evaporate which left a visible soap-scum layer upon the sacrificial area. Thus, when beginning the careful peeling process of each layer, this sacrificial area released with little to no effort and allowed for the careful peeling to continue within the patterned area without the layer lifting from the bottom pattern. Minor de-moulding damage occurred when carefully peeling the first, soft 20:1 cladding layer. Figure 4.18 shows the de-moulding damage. The damage is close to the inlet/outlet and axis of rotation, thus it is suspected that this region was not properly partially cured due to PDMS being pushed back out of the cavity from thermal expansion. Alternatively, this region of the master pattern may not have had release agent properly applied to it.

Figure 4.18: During the careful peeling of the first layer, minor de-moulding damage occurred. Due to the location, the damage is suspected to be from thermal expansion pushing PDMS back out and curing less in that region.
The subsequent layers were successful and the first functional prototype was produced. Figure 4.19 shows images of the resultant prototypes. Figure 4.19 a) and c) show flat views of both illuminated prototypes while b) and d) show the prototypes in bending to demonstrate their flexibility. There exists some bubbles in the final cladding layer of the dome-MOS prototype which can be attributed to a mistake by the experimenter. A mistake was made in measuring the amount of required PDMS for the final layer. The cavities created by the MOSs upon the previous master pattern were unaccounted for. In an attempt to hastily solve this issue the excess PDMS from the previous cladding layer, which had the same 20:1 mixing ratio, was used to fill the remainder of the mould cavity. This PDMS sat at room temperature for over 5 hours during the fabrication of the first and second layers. The recommended pot-life for PDMS is 2 hours before cross-linking begins to occur. It was slightly more difficult to inject this PDMS compared to previous PDMS, indicating that the viscosity of this PDMS was higher. A higher viscosity liquid requires a longer spin time to completely remove bubbles. The 20 minute spin time was not enough to remove 100% of bubbles with this new viscosity; therefore, bubbles are found embedded within the final product.

![Image of prototypes](image_url)

Figure 4.19: Images of the first illuminated 3-layer prototypes. It was very difficult to prevent dust from being attracted to the prototype’s surfaces which can be seen in the photographs. a) Flat view of the prototype with internal dome MOSs. The domes are difficult to see due to the low $\Delta \eta = 0.007$. b) Dome prototype in bending to demonstrate flexibility. c) Flat view of the prototype with internal wedge MOSs. The wedges are nearly impossible to see. d) Wedge prototype in bending to demonstrate flexibility.

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7 The 2 hour pot-life is for 10:1 ratio PDMS, 20:1 ratio PDMS likely has a longer pot-life due to having less curing agent.
It was very difficult to see the internal MOSs in the prototypes, especially the wedge MOSs. Figure 4.20 attempts to visualize the MOSs in the dome prototype by sending light through the main illuminating surface and seeing the shadows formed in the background. To further visualize the existence of three layers and internal MOSs food colouring was added to the core layer in the next trials.

Figure 4.20: Light is shown through the prototype with dome MOSs to be capable of visibly seeing the internal MOSs via shadows in the background.

Trial 3

The third trial used a 10:1 base-to-agent mixing ratio for all three layers because food colouring was added to the core layer for visualization of the internal MOSs and existence of three layers. Figure 4.21 shows the resultant illuminating prototypes where a single drop of green food colouring was added to each illuminator’s core layer. When originally mixing the PDMS and green food colouring for the core layer, the mixture appeared quite green. However, once the mixture was turned into a thin layer and cured, most of the green colour had disappeared. Many bubbles appeared in the dome-MOS prototype and one very large bubble appeared in the wedge-MOS prototype. There are two educated guesses as to why these bubbles appeared. The first guess is the addition of food colouring which has water and propylene glycol in
the ingredients. These ingredients may have interacted with the heat or PDMS and produced gasses during thermal curing. The second guess is that air from below the bottom pattern made its way into the layers during the thermal cure. Figure 4.22 shows how the two bottom flat PDMS master patterns eventually curled after multiple trials of being heated and cooled. These patterns would no longer stay adhered and flush to the smooth PETG sheet. Modifications to the mould and mixing process were made for the final trial to produce a final set of coloured prototypes.

**Trial 4**

For the last trial, the bottom PDMS master patterns were replaced with a flat PMMA master. No release agent was applied to this PMMA master since previous experience showed that PDMS does not adhere to PMMA masters as much as it does to PDMS masters. This time, 10 total drops of red food colouring was first added to the PDMS base and then left in an oven at 40 °C for 48 hours to allow the water and propylene glycol to evaporate out. This evaporation had also removed much of the red hue from the PDMS-base and food colouring mixture. This mixture was then cooled to room temperature and then mixed with the curing agent to create a 10:1 ratio core layer. The new PMMA bottom master proved successful in preventing the
Figure 4.22: Image of the bottom flat PDMS master patterns curling after being heated and cooled multiple times.

mass of bubbles from finding their way into the layers. However, the sacrificial areas were riddled with bubbles likely due to the inability to seal the bottom PMMA master against the aluminium. This area was cut away, but some of these bubbles appeared in the main regions of the final product. Figure 4.23 shows the resultant prototypes where the MOSs are clearly visible, especially in the dome-MOS illuminator. Due to the red food colouring, the light from the embedded LEDs is quickly absorbed.

4.4 Discussion - Prototype Functionality

Figures 4.19, 4.21, and 4.23 each demonstrate the flexibility and illumination of PDMS waveguide sheets. Figure 4.24 also demonstrates these properties where it is clearly visible that even in bending the illumination continues through to the opposite end of the light source. Unfor-
Figure 4.23: Illuminating prototypes where 5 drops of red food colouring was added to each prototype’s core layer of PDMS. Bubbles appeared in the prototypes from poor sealing of the PMMA bottom master. a) Flat view of dome-MOS prototype. b) Dome prototype in bending to demonstrate flexibility. c) Flat view of wedge-MOS prototype. d) Wedge prototype in bending to demonstrate flexibility.

Fortunately, this is more so due to the low $\eta$ of air ($\eta_{\text{air}} \approx 1.0$) and not the intended cladding-core-cladding interfaces. The bent illuminators still function through light internally reflecting off the cladding-air interface which has a $\Delta\eta \approx 0.45$. Due to the low $\Delta\eta = 0.007$ of these prototypes, much of the light quickly escapes the core layer during bending and enters the cladding.

Section 3.2 discussed the many essential aspects which must be present for a functional illuminator. These aspects include the $\Delta\eta$ between core and cladding layers, the quality and size of the MOS master patterns, and the embedded light source. The $\Delta\eta$ can be improved by adding high $\epsilon_r$ nano-particles to increase the refractive index of PDMS for the core layer. The addition of these nano-particles proved to be difficult where aggregates always formed, creating an opaque material. However, existing literature, such as the work done by Little [74], has shown that increasing the $\eta$ of PDMS using nano-particles is indeed possible. The quality of MOS patterns can also be improved through use of high-quality micro machining or photolithography, depending on the size and intended application of the optical device. A large array of smaller MOSs will produce better uniformity, as detailed in Section 2.4.5. Finally, the embedded light source could be improved to supply better initial uniform illumination to the first MOSs the light will interact with. Figure 4.25 shows that when a flexible light source is embedded, it will flex and bend with the device. A light source could be tailored specifically for illuminators to be very thin, uniform, and have similar bending capabilities to that of PDMS.
Figure 4.24: Example of PDMS-based illuminator flexibility. Since the optical device uses a monolithic design where three layers of PDMS are strongly bonded, the limits to the flexibility are that of the PDMS material.

Through additional research and experimentation, these essential aspects can be added to the fabrication methodology to produce highly functional and efficient prototypes. Section 5.3 in the final Chapter discusses some recommendations for future work involving this research.

Figure 4.25: Demonstrated flexibility of illuminators with an embedded flexible LED strip.

4.4.1 Discussion - Feasibility of The Fabrication Methodology

Disregarding the expected poor functionality of the illuminating prototypes, they have still been fabricated using a methodology capable of creating multiple layers with internal MOSs. Therefore, the resultant 3-layer illuminator prototypes presented in Section 4.3.3 have demonstrated
the feasibility of the proposed fabrication methodology detailed in Chapter 3. The existence of three separate thin PDMS layers with internal MOSs embedded between two of the layers proves that the centrifugal casting and partial curing techniques are capable of producing robust and complex optical devices in a timely manner. Figure 4.26 images a) and b) show photographs of the existence of three layers in trial #4. The food colouring was used specifically to demonstrate this, as without colouring the three layers were difficult to see. Figure 4.26 image c) shows a picture using a camera down a 5x microscope lens\(^8\) of a prototype from trial #2. This trial did not have food colouring in the core layer, yet under microscope it is clear that the optical device consists of three separate layers. Future research is required to investigate the resultant grain boundaries of the material and if centrifugal casting or partial curing affects it.

Figure 4.26: Images showing the existence of three different bonded PDMS layers. a) Edge of one of the illuminators from trial #4. b) Cross Section of the cut-away sacrificial area. c) 5x transmitted optical microscope lens image of the cross Section cut-away sacrificial area from trial #2.

Figure 4.27 provides proof of the existence of wedge and dome MOSs in the illuminator prototypes. The internal MOSs are visible to the naked eye within the food colouring pro-

\(^8\) Because the layers were relatively large at 1-2mm thick and the microscope’s camera took images at an additional 2x zoom, it was not possible to view all three layers in a single microscope image capture.
Chapter 4. Feasibility Study - Fabrication of Functional Prototypes

Prototypes from trial #4 which can be seen in the close-up images of Figure 4.27 a) and c). The internal MOSs in the transparent prototypes from trial #2 are difficult to see with the naked eye, however using a transmitted optical microscope these features are clearly visible in Figure 4.27 images b) and d). Both the microscope camera lens and prototypes had dust upon them. It appears that PDMS-based devices quickly attract dust upon the surface. This attraction is also true when performing the careful peeling technique where dust can actually accumulate between layers. This could be prevented further by performing this technique in a clean room. The partial curing and careful peeling techniques which create a new master pattern upon a partially cured layer have successfully created internal MOSs which are inherently protected by the outer cladding regions. Future research is required using different release agents and environments for PDMS-on-PDMS soft-lithography and the partial curing technique to observe if the quality of MOSs improves.

Figure 4.27: Images showing the existence of MOSs between PDMS layers. a) Close-up of wedges from trial #4. b) Microscope image of a wedge from trial #2 c) Close-up of domes from trial #4. d) Transmitted optical microscope image showing the edges of two domes within the illuminator from trial #2.
4.5 Discussion - Fabrication Speed and Industry Potential

This new methodology has improved the fabrication time compared to existing literature techniques. Traditionally, to create a 3-layer illuminator with MOSs present between two layers, a lengthy vacuum chamber degassing is performed to remove bubbles from the mixed PDMS before it is spin coated upon master patterns into thin films. After the thin films are fully cured, the layers are removed and the positive and negative MOSs are precisely aligned using optical alignment techniques. The layers are then bonded using a technique such as plasma bonding to create a multi-layered optical device. This approach can be very length and overly complex, however some fabrication time can be saved by spin coating and curing all required layers at once. Most of the fabrication time in the traditional approach is present in the vacuum chamber degassing and layer alignment steps. In the new fabrication methodology presented in Chapter 3, the centrifugal casting technique quickly removes bubbles and is capable of filling very thin mould cavities which have a pre-set thickness. Thin cavity moulding combined with the partial curing and careful peeling techniques prevent the need to precisely align and bond multiple patterned PDMS layers. Instead, a previous partially cured layer is used as a new master pattern for the subsequent layer and new material is centrifugally cast upon it. Overall, this is a considerable reduction of fabrication time and complexity with the added bonus that bonding by partial curing is the strongest of bonding techniques [94].

In experimental trials, the bulk of fabrication time and complexity was present in the assembly and disassembly of the moulds. Working with 64 screws and slowly injecting/spinning PDMS for each layer took more time than the actual low-temperature partial cures used. It is also possible to use higher temperature cures to reduce curing time if measures are taken to prevent or calibrate for the PDMS shrinkage and mould thermal expansion. Furthermore, with a low spin rate of 1000 RPM, 20 minutes was required to fully remove bubbles from each layer. The work done by Mazzeo et al. [101] has shown that this spin time is significantly reduced at higher spin rates. Therefore, the overall fabrication time of this methodology still has much room for improvement. The reduction in overall complexity and time creates potential for this fabrication methodology to be used in industry. With the essential aspects described in Section 3.2, hydraulic-clamped moulds and automated processes can be utilized to quickly fabricate complex multi-layered optical devices. The remaining complexity now resides in the design of MOSs and fabrication of the master patterns used in the methodology.
4.6 Concluding Remarks

The illuminating prototypes produced in this chapter are not ideal, however they do display some functionality and clearly consist of three different PDMS layers with MOSs embedded between the top core-cladding interface. It was discovered during experimental trials with the large area centrifugal mould that the technique to hold master patterns in place has a limitation. Larger elastomeric master patterns can sag in the middle from gravity if only the outer perimeter of the master pattern is held down. The sagging creates an air gap between the mould surface and the master pattern which will expand and worsen during the thermal curing stage. In trials this was solved by adding smooth surfaces to the mould top and bottom for the PDMS master patterns to stick to via van der Waals force and suction. For larger area master patterns, a vacuum may be used to hold the pattern to the mould top. Alternatively, flexible steel mesh could be embedded within the master patterns with an electro magnet present in the mould top to keep them in place and then quickly release the master when needed.

In conclusion, the experiments presented in this chapter have proved the feasibility of the proposed fabrication methodology. Additional research is required to optimize the process and improve the quality of optical devices created which is explained in Section 5.3. This research has presented a fabrication methodology with the potential to fabricate complex multi-layer thin and flexible optical devices with internal optical elements in a simple streamlined build-by-layers approach.
Chapter 5

Thesis Summary, Conclusions, and Future Work

5.1 Thesis Summary

A novel methodology for the fabrication of light concentrating (collectors) or light diffusing (illuminators) multi-layer flexible optical devices with internal micro-optical structures (MOSs) has been presented, detailed, and tested for feasibility in this thesis. Polydimethylsiloxane (PDMS) was chosen as the flexible material of choice due to its desirable properties as a transparent, flexible and organic thermosetting polymer which is detailed in Section 2.6.2. The basic properties of light are explained in Section 2.2 to develop an understanding of physical optical device constraints. A literature review of existing flexible optical devices and PDMS-based fabrication is detailed in Sections 2.3 to 2.7. The proposed fabrication methodology is presented in Chapter 3 where Figure 3.6 illustrates the concept in detail. The fabrication methodology uses centrifugal force to rapidly fill and degas a thin mould cavity. Elastomeric master patterns are present within the mould cavity to replicate MOSs via the soft-lithography technique detailed in Section 2.7.1. To create internal MOSs a layer is partially cured and the elastomeric master pattern is then carefully peeled from the layer’s top surface. Additional mould wall thickness is added and the new MOS-patterned partially cured surface then acts as the new master pattern for the subsequent layer. The process is repeated for the desired number of layers until finally performing a full cure.

Chapter 4 details the proof of concept experiments using the proposed fabrication methodology. Section 4.3.1 details the main experiment where a large aluminium centrifugal mould was fabricated and tested. Several 3-layer illuminating prototypes were fabricated to demonstrate the feasibility of the proposed methodology. The goal of the experiments were to prove
the existence of 3 different bubble-free PDMS layers with internal MOSs embedded between one of the core-cladding interfaces. By utilizing a PDMS base-to-agent technique, $\Delta \eta = 0.007$ was available for core-cladding waveguiding using total internal reflection (TIR). With such a low $\Delta \eta$ it was difficult to visibly see the internal MOSs and existence of 3 different layers. Therefore, for the last trials food colouring was added to the core layer to clearly see MOSs. Pictures and microscope images are presented in Section 4.4.1. The feasibility of the proposed fabrication methodology has been proven, however there is much work left in optimizing the methodology and improving the quality of flexible optical devices produced which is explained in the following section.

## 5.2 Concluding Comments

The objective of this research project has been to develop a feasible scalable fabrication methodology to create multi-layered, large area PDMS sheets with internal optical elements which may act as either illuminators or collectors. Through vast experimentation the feasibility of a novel centrifugal fabrication methodology was proven in this research project. The fabrication methodology is capable of creating large area and multi-layered PDMS optical devices with MOSs embedded between layers in a relatively simple streamlined build-by-layers approach. The methodology prevents the need for the precise alignment and bonding of multiple thin layers which would have been required using traditional techniques to create internal optical elements. Internal MOSs in optical devices is a new contribution to science which opens up a new range of applications for flexible optical devices since these delicate structures are now protected by the cladding layer(s). This novel methodology would not have been possible without performing multiple iterations of different moulds to develop a deep understanding of PDMS-based fabrication. Appendix B briefly summarizes each iteration and the issues which occurred, leading up to the proposed fabrication methodology presented in Chapter 3. Appendix C briefly details the design of the aluminium centrifugal mould assembly used in Section 4.3.1. With further process optimization, a greater $\Delta \eta$ between PDMS layers, and better MOS patterns, robust flexible illuminators/collectors can be fabricated in a timely manner using this fabrication methodology. Applications for these functional optical devices are for surfaces that change and vary with use, such as a runner’s jacket for collecting solar energy or illuminating a dark night. The fabrication methodology developed in this research can also be used for many other types of flexible optical devices with a single layer or many layers because of the build-by-layers approach.
5.3 Recommendations for Future Work

Section 3.4 explained the potential limitations of the proposed fabrication methodology. These limitations are essentially topics for future work, some of which are briefly described in this section. As previously mentioned, this research is essentially a proof of concept for the proposed fabrication methodology presented in Chapter 3. The experiments detailed in Chapter 4 have proven the feasibility of the methodology to create multi-layer PDMS optical devices with internal MOSs between layers. There is still much work in the optimization of the methodology and the PDMS material used. The first optimization suggestion is to simply increase the RPMs of the centrifugal mould. Mazzeo et al. [101] have data relating to the required spin time at different spin rates. Their data shows that as the spin rate increases the time required for complete bubble removed drops significantly. Therefore, the overall fabrication time can be greatly reduced by increasing the spin rate due to the multiple layers that must be spun. To safely increase the spin rate, the mould must be designed stronger and be accurately balanced.

Section 2.6.3 and 3.2.1 explained how the refractive index, $\eta$, of PDMS can be increased by over 0.1 with the addition of nano-particles with a high dielectric constant. Such a large $\Delta\eta$ is ideal for the interaction of light upon MOSs and the core-cladding interface. It may be possible to simply add commercial surface-modified titanium dioxide (TiO$_2$) nano-particles to the PDMS pre-polymer which can be used as the core layer material in illuminators and collectors. Further research and experimentation is required to find compatible surface-modified TiO$_2$ nano-particles. As a suggested start, US Research Nanomaterials, Inc$^1$ has several surface-modified TiO$_2$ nano-particles available, such as one which is coated with silicone oil.

Using centrifugal force to insert and simultaneously degas the pre-polymer within the mould cavity has saved a considerable amount of time during fabrication compared to the traditional vacuum chamber degassing used in existing literature. The real time-sink for PDMS-based fabrication is the thermal curing of the polymer. In this research, lower curing temperatures ($25 - 65 \, ^\circ\text{C}$) with longer cure times (1.5–48 hrs) were used to avoid PDMS shrinkage. When multiple layers of PDMS are cast and then partially thermally cured one after the other, the time required for each layer adds up. Section 2.7.1 described how Wong [69] found there exists a gel point where PDMS transitions from a liquid to a solid. The temperature at the gel point dictates the amount of shrinkage which may occur. Therefore, it would be interesting to see a reduction in fabrication time from utilizing this gel point. After the gel point is reached, the curing temperature can be increased significantly for a rapid partial cure of the layer, which may reduce the overall fabrication time. Additional to the gel point, the fabrication time can be reduced by thermally curing layers while the mould is spinning. Near the end of the required

$^1$ Company website: www.us-nano.com
spin time the temperature can be increased, thus saving the time to stop the spinning mould and transfer it to a heat source. There may also be other beneficial effects from thermally curing while spinning. The increase in pressure from spinning could even prevent the shrinkage issues with curing PDMS at higher temperatures or may prevent PDMS escaping back out the mould due to thermal expansion effects; only future research can unlock this answer.

In this research project PDMS was used as the elastomeric master pattern material due to availability. Other flexible or elastomeric master pattern materials may exist for use with this fabrication methodology. There may even exist an ideal material which PDMS does not adhere to, preventing the need for a release agent upon master patterns. Additionally, after many trials of heating and cooling the same PDMS master patterns, they began to curl slightly. It is unknown whether this curling was induced by the sagging issues which occurred from the PDMS master patterns not adhering to the mould surfaces in the first trial experiments of Section 4.3.3. Therefore, further research is also required to observe the effects of re-using the same PDMS master patterns.

Finally, future research is necessary to observe the effects of large centripetal force vectors upon MOSs, especially if thermal curing is performed while spinning the mould. To observe this, a comparison can be made between the MOS dimensions of master patterns with the replicated MOS dimensions. The dimensions may be skewed away from the axis of rotation. In the topic of specifically studying MOS replication, it would also be beneficial to quantify how small of MOSs can be filled and replicated using centrifugal casting. Since a closed mould is used with this methodology, the technique detailed in Section 2.7.1 which uses a compatible solvent to dilute PDMS for filling small nano feature cavities cannot be used because the solvent must evaporate out of a large open area. Undiluted PDMS with larger centrifugal forces may be capable of easily filling nano-size cavities.

There is much left to discover, learn and optimize using this fabrication methodology. With further research, this methodology could be capable of quickly producing very complex flexible optical devices. Since this methodology can create MOSs which are internal to the device and inherently protected, robust illuminators and collectors are possible for a wide range of applications.
Bibliography


Appendix A

Equations

A.1 Fresnel Equations

Augustin-Jean Fresnel deduced the Fresnel equations which describe the behaviour of light when moving between media of differing refractive indices [39]. The Fresnel equations describe the fraction of light which is reflected and the fraction which is refracted between media. Polarization has an effect on the behaviour of incident light which can be split into parallel (p-polarized) and perpendicular (s-polarized) light relative to the plane of incidence.

The fraction of incident light that is reflected is defined as the reflectivity, $R$, while the fraction that is refracted is defined as the transmittance, $T$. The reflectance for s-polarized light for non-magnetic media is given by:

$$R_s = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_i} \right|^2 = \frac{n_1 \cos \theta_i - n_2 \sqrt{1 - \left( \frac{n_1}{n_2} \sin \theta_i \right)^2}}{n_1 \cos \theta_i + n_2 \sqrt{1 - \left( \frac{n_1}{n_2} \sin \theta_i \right)^2}}$$

and the reflectance for p-polarized light is given by:

$$R_p = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_i} \right|^2 = \left| \frac{n_1 \sqrt{1 - \left( \frac{n_1}{n_2} \sin \theta_i \right)^2} - n_2 \cos \theta_i}{n_1 \sqrt{1 - \left( \frac{n_1}{n_2} \sin \theta_i \right)^2} + n_2 \cos \theta_i} \right|^2$$

finally, using the conservation of energy, the transmittances are given by:
A.2 Brewster’s Angle

Brewster’s angle is a special angle of incidence where light with a particular polarization is fully transmitted through a transparent dielectric medium without reflection occurring. Brewster’s angle is found within Fresnel equations (appendix A.1) where at a given $\eta_1$ and $\eta_2$, the value of the p-polarized reflectance goes to zero and a p-polarized incident ray is purely refracted. It is given by:

$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right)$$

A.3 Maxwell’s Equations

Maxwell’s equations are a set of partial differential equations that form the foundation of classical electrodynamics, classical optics, and electric circuits. In a vacuum with no charges or currents Maxwell’s wave equations reduce to:

$$\frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} - \nabla^2 \mathbf{E} = 0$$

$$\frac{1}{c^2} \frac{\partial^2 \mathbf{B}}{\partial t^2} - \nabla^2 \mathbf{B} = 0$$

which identify:

$$c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} = 2.99792458 \times 10^8 \text{ m s}^{-1}$$

with the speed of light in free space. In materials with relative permittivity, $\varepsilon_r$, and relative permeability, $\mu_r$, the phase velocity of light becomes
A.4 Fermat’s Principle

Fermat’s principle, also known as the principle of least time, is that the path taken between points A and B by a ray of light will be the path that can be traversed in the least amount of time. This principle is sometimes taken as the definition of a ray of light; heavily used in optics. Fermat’s principle can be used to describe the properties of light rays reflected off mirrors, refracted through different media, or undergoing total internal reflection and is used to derive Snell’s law of refraction as well as the law of reflection. The amount of time $T$ a point of the electromagnetic wave needs to cover between points A and B is given by:

$$T = \int_{t_0}^{t_1} dt = \frac{1}{c} \int_{t_0}^{t_1} \frac{c}{v} \frac{ds}{dt} dt = \frac{1}{c} \int_{A}^{B} n \, ds$$

where $c$ is the speed of light in vacuum, $ds$ an infinitesimal displacement along the light ray, $v = \frac{ds}{dt}$ is the speed of light in a medium and $\eta$ is the refractive index of that medium.
Appendix B

Path to Discovery

Many experiments, failures and iterations were required to develop a feasible fabrication method for creating multi-layered complex waveguide devices. After a period of initial research on illuminator/collector polydimethylsiloxane (PDMS)-based fabrication, practical application and experimentation was necessary to develop a deeper understanding of the potential fabrication issues which may arise using PDMS for such devices. Below is a summary of each poly(methyl methacrylate) (PMMA) mould iteration which eventually led to the discovery of a multi-layer centrifugal casting approach. A description, computer-aided design (CAD) models, and the pros/cons of each iteration are summarized.

Iteration 0

Description: A naïve single-layer approach intended to supply insight for fabricating with PDMS (Figure B.1). Many PDMS fabrication issues were identified for the subsequent iterations.

Table B.1: Mould iteration 0 pros and cons

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple pattern alignment</td>
<td>Bubbles</td>
</tr>
<tr>
<td>Accurate layer thickness</td>
<td>Difficult to release</td>
</tr>
<tr>
<td></td>
<td>Sealing issues/leaking</td>
</tr>
<tr>
<td></td>
<td>Difficult to insert pre-polymer</td>
</tr>
<tr>
<td></td>
<td>No layering capabilities</td>
</tr>
</tbody>
</table>
Iteration 1

Description: A mould which fixes the sealing and releasing issues by adding gaskets and an air-release system (Figure B.2). The mould releases from the pattern before the pattern demoulds from the layer’s featured surface improperly and causes damage. The air release turned out to be unnecessary as the holes had prevented the previous suction seal to make separating the mould easier. This iteration is also built to allow for any layer thickness by using thin spacer shims. The O-rings used to seal the mould ended up trapping additional air, which once heated the air expanded and escaped into the layer.

Table B.2: Mould iteration 1 pros and cons

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple pattern alignment</td>
<td>Bubbles</td>
</tr>
<tr>
<td>Accurate layer thickness</td>
<td>No layering capabilities</td>
</tr>
<tr>
<td>Releases easily</td>
<td>Difficult to insert pre-polymer</td>
</tr>
<tr>
<td>Seals well/no leaks</td>
<td></td>
</tr>
</tbody>
</table>

Iteration 2

Description: A mould where an inlet and outlet was added on both ends of the mould for PDMS insertion (Figure B.3). Injection and a vacuum were used to push or pull PDMS into the thin cavity. A PDMS master pattern was used to act as a gasket with 0.20mm of compres-
Sets of thin shims and flat gaskets were used to create multiple layers using the partial curing technique found in literature. The first successful multi-layered prototype was fabricated using the partial curing and careful peeling techniques. The prototype had an embedded light emitting diode (LED) and needed about 10 times the required amount of PDMS to push the newly formed bubbles (formed when PDMS laps over itself and features) out, and small ones still remained. It appeared that bubbles were unavoidable.

**Iteration 3**

**Description:** After bubbles appeared to be unavoidable when using closed mould cavities, a new technique was required. Centrifugal force was already being used with previous mould iterations to quickly degas the pre-polymer before inserting it; thus a new idea occurred. After the proof of concept experiment described in section 3.3.2 and shown in Figure 3.8 was performed, the term centrifugal casting was discovered from the work done by Mazzeo [92]. A new complex mould was then designed, built, and tested which had all the working features of previous moulds with the ability to be spun by a spindle for centrifugal casting (Figure B.4).
Figure B.3: CAD model of iteration 2 with added features (left). First multi-layered prototype with embedded LED (right).

Table B.3: Mould iteration 2 pros and cons

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple pattern alignment</td>
<td>Bubbles</td>
</tr>
<tr>
<td>Accurate layer thickness</td>
<td></td>
</tr>
<tr>
<td>Releases easily</td>
<td></td>
</tr>
<tr>
<td>Seals well/no leaks</td>
<td></td>
</tr>
<tr>
<td>Capable of multiple layers</td>
<td></td>
</tr>
<tr>
<td>Easy to insert pre-polymer</td>
<td></td>
</tr>
</tbody>
</table>

During the first test, the first two out of three layers had worked very well with no bubbles present after partial curing and preparing for subsequent layers. Unfortunately, when spinning at 3000 RPM for the third layer, the mould broke free from the spindle and crashed against the protective wooden shield.

### B.0.1 Conclusion

The final result from iteration 3 had proven enough feasibility in the centrifugal concept to invest in a much stronger and larger mould for proving the overall feasibility of the fabrication methodology detailed in section 4.3. Hands-on experience was required to understand waveguide fabrication with PDMS. The fabrication methodology still requires much optimization to improve the fabrication speed, quality and scale.
Figure B.4: CAD model of iteration 3 for centrifugal casting (left). Fabricated mould (right).

Table B.4: Mould iteration 2 pros and cons

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple pattern alignment</td>
<td>Mould strength during spinning</td>
</tr>
<tr>
<td>Accurate layer thickness</td>
<td></td>
</tr>
<tr>
<td>Releases easily</td>
<td></td>
</tr>
<tr>
<td>Seals well/no leaks</td>
<td></td>
</tr>
<tr>
<td>Capable of multiple layers</td>
<td></td>
</tr>
<tr>
<td>Easy to insert pre-polymer</td>
<td></td>
</tr>
<tr>
<td>No bubbles and does not require prior degassing of the pre-polymer</td>
<td></td>
</tr>
</tbody>
</table>
Appendix C

Centrifugal Moulding System CAD & Drawings

The following pages are CAD drawings from Solidworks Student Edition. Some design, assembly and dimensions are not detailed within these drawings compared to traditional engineering CAD drawings. Instead, the following CAD drawings are intended for design insight and to give the reader an idea of how such a mould system was fabricated using a computerized numerical control (CNC) machine. Table C.1 lists the tools used in the fabrication of the centrifugal moulding system presented in section 4.3.1. Figure C.1 illustrates the full system CAD in Solidworks. A DXF file was used with a CNC machine to fabricate each piece. Since many pieces were very similar, fabrication time was saved by machining multiple pieces clamped together at once.
Table C.1: Tools used in centrifugal mould system fabrication

<table>
<thead>
<tr>
<th>Tool</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drill #7</td>
<td>0.201”</td>
</tr>
<tr>
<td>Drill #10</td>
<td>0.1935”</td>
</tr>
<tr>
<td>Drill #18</td>
<td>0.1695”</td>
</tr>
<tr>
<td>Drill #25</td>
<td>0.1495”</td>
</tr>
<tr>
<td>Drill #30</td>
<td>0.1285”</td>
</tr>
<tr>
<td>Drill 33/64</td>
<td>0.5156”</td>
</tr>
<tr>
<td>Tap 10-32</td>
<td></td>
</tr>
<tr>
<td>Flat End-mill</td>
<td>1/8”</td>
</tr>
</tbody>
</table>

Figure C.1: CAD of Centrifugal Moulding System.
Bill of Materials

<table>
<thead>
<tr>
<th>ITEM NO.</th>
<th>PART NUMBER</th>
<th>QTY.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2&quot; Bearing</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Bearing Block</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1/2&quot; Drive Shaft</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Shaft Collar</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>8-32 Screw</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>Propeller Base</td>
<td>1</td>
</tr>
</tbody>
</table>

Some design, assembly and dimensioning are not detailed in the following drawings. These drawings are for design insight only.

MATERIAL:

SOLIDWORKS Student Edition.
For Academic Use Only.
Some design, assembly and dimensioning are not detailed in the following drawings. These drawings are for design insight only.

### Bill of Materials

<table>
<thead>
<tr>
<th>ITEM NO.</th>
<th>PART NUMBER</th>
<th>QTY.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pattern Holder</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Cladding Spacer</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Core Spacer</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Mould Top</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>PDMS Pattern</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>1/4&quot; Steel Dowel</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>7/8&quot; 10-32 Screw</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>Tube Flange</td>
<td>2</td>
</tr>
</tbody>
</table>
- Symmetry around centre
- 0.16" Thick Stock
- Perimeter Hole Spacing is 20mm

MATERIAL:

TITLE:
From MESc Thesis:
PDMS Waveguide Sheets

AUTHOR:
Robert Green

NOTES:
SOLIDWORKS Student Edition.
For Academic Use Only.

Units in inches unless otherwise stated

SCALE: 1:2
- Symmetry around centre
- 0.08" Thick Stock
- Perimeter hole spacing is 20mm

MATERIAL:

TITLE:
From MSc Thesis:
Fabrication of Large Area Flexible PDMS Waveguide Sheets

AUTHOR:
Robert Green

SCALE:
1:2

NOTES:
SOLIDWORKS Student Edition.
For Academic Use Only.
Appendix D

Centrifugal Moulding System FEA

D.0.1 Study Notes

- Symmetry used for simplification.

- Adding bolts was found to add little to the overall results while causing longer simulation times. A contact bond was used instead.

- Mass of bolts, patterns and PDMS added as remote mass ($\approx 0.388\,\text{kg}$) to simulate the heaviest possibility.

- Yield strength of 6061 aluminium purchased was 35 000 psi while the study uses the available 6061 with yield strength of 33 000 psi.

- Angular acceleration was ignored as the system will be slowly ramped up and down on velocity.

D.1 Study Set-up

Using Solidworks Simulation, a study was prepared to determine the maximum revolutions per minute (RPM) the centrifugal moulding system could withstand before plastic deformation occurs. This mould has been designed to spin between 1000-2000RPM and thus requires a high factor of safety to ensure the mould can withstand these speeds and any other potential influence while in operation. Figure D.1 shows the overall set-up where symmetry has been utilized and only the driving bolts are simulated. Nonlinear-static with ten total steps was used to obtain accurate results.
D.1.1 Material

Table D.1 details the material properties of the 6061 T4 aluminium which best matched the purchased aluminium. All components in this study were modelled as 6061 T4. However, in reality the drive shaft and clamp fixture are steel.

Table D.1: 6061 T4 material properties

<table>
<thead>
<tr>
<th>6061 T4 Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield strength</td>
<td>2.27527e+008 N/m²</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>2.4e+008 N/m²</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>6.9e+010 N/m²</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.33</td>
</tr>
<tr>
<td>Mass density</td>
<td>2700 kg/m³</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>2.6e+010 N/m²</td>
</tr>
</tbody>
</table>
D.1.2 Loads and Fixtures

The table below lists the loads and fixtures used in the FEA study.

<table>
<thead>
<tr>
<th>Type</th>
<th>Visual</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Hinge</td>
<td><img src="image1.png" alt="Image" /></td>
<td>Fixed hinge simulates the drive-shaft which would be present.</td>
</tr>
<tr>
<td>Symmetry</td>
<td><img src="image2.png" alt="Image" /></td>
<td>Applied to all faces at the symmetry plane.</td>
</tr>
<tr>
<td>Centrifugal Load</td>
<td><img src="image3.png" alt="Image" /></td>
<td>Angular velocity applied to clamp which is fixed to the drive shaft.</td>
</tr>
<tr>
<td>Remote Mass</td>
<td><img src="image4.png" alt="Image" /></td>
<td>Includes the mass of both patterns, all bolts and a full cavity of PDMS</td>
</tr>
<tr>
<td>Gravity</td>
<td><img src="image5.png" alt="Image" /></td>
<td>Gravity added at $9.81m/s^2$ in the vertical direction.</td>
</tr>
</tbody>
</table>

D.1.3 Mesh

Figure D.2 shows the resultant mesh visual using a control mesh around the holes. Table D.2 lists the mesh parameters and resultant nodes/elements.
Figure D.2: Resultant mesh visual using a control mesh around the holes.

Table D.2: Mesh parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh Type</td>
<td>Solid Standard</td>
</tr>
<tr>
<td>Jacobian Points</td>
<td>4</td>
</tr>
<tr>
<td>Element Size</td>
<td>10.5278 mm</td>
</tr>
<tr>
<td>Total Nodes</td>
<td>61437</td>
</tr>
<tr>
<td>Total Elements</td>
<td>37688</td>
</tr>
<tr>
<td>Mesh Control Element Size</td>
<td>4.5mm</td>
</tr>
</tbody>
</table>

D.1.4 Study Results

Table D.3 lists the study results at 1000, 2000, 3000, and 4000 RPM. Plastic deformation begins to occurs between 3000 and 4000 RPM. For safety purposes, the factor of safety should stay above 2.0 in these experiments, therefore the mould should not be spun at speeds greater than 2000 RPM.
### Table D.3: Study results

<table>
<thead>
<tr>
<th>Spin Speed</th>
<th>Max von Mises Stress</th>
<th>Factor of Safety</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 RPM</td>
<td>6.985e+007 N/m$^2$</td>
<td>3.26</td>
</tr>
<tr>
<td>2000 RPM</td>
<td>1.091e+008 N/m$^2$</td>
<td>2.08</td>
</tr>
<tr>
<td>3000 RPM</td>
<td>1.978e+008 N/m$^2$</td>
<td>1.15</td>
</tr>
<tr>
<td>4000 RPM</td>
<td>3.145e+008 N/m$^2$</td>
<td>0.72</td>
</tr>
</tbody>
</table>
# Curriculum Vitae

<table>
<thead>
<tr>
<th>Name:</th>
<th>Robert Green</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Post-Secondary Education and Degrees:</strong></td>
<td>The University of Western Ontario London, ON 2010 – 2014 B.E.Sc</td>
</tr>
<tr>
<td></td>
<td>University of Western Ontario London, ON 2014 – 2016 M.E.Sc</td>
</tr>
<tr>
<td><strong>Honours and Awards:</strong></td>
<td>Graduate Teaching Assistant (GTA) Award 2014 – 2016</td>
</tr>
<tr>
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<td>Canadian Manufacturers &amp; Exporters Scholarship 2013</td>
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<tr>
<td><strong>Related Work Experience:</strong></td>
<td>Teaching Assistant The University of Western Ontario 2014 – 2016</td>
</tr>
<tr>
<td></td>
<td>Advanced Feature Development Internship Automotive Research and Development Center, Windsor, ON &amp; Chrysler Technology Center, Auburn Hills, MI (Joint office) 2012 – 2013</td>
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</table>

**Publications:**

R. Green, G. K. Knopf, and E. Bordatchev, "Fabrication of large area flexible PDMS waveguide sheets", *Proc. SPIE 9759, Advanced Fabrication Technologies for Micro/Nano Optics and Photonics IX*, 97590U (March 14, 2016); DOI: [10.1117/12.2208789](https://doi.org/10.1117/12.2208789)