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Ultrashort Pulse Laser Scribing of Thin Flexible Glass

by

Adam R. Collins, B.Sc.

A thesis submitted to the National University of Ireland, Galway, in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

National Centre for Laser Applications,
School of Physics,
National University of Ireland, Galway.

Academic Supervisor:
Dr. Gerard M. O’Connor

October 2015
Is fada an bóthar nach mbíonn casadh ann.

Seanfhocal Gaeilge

I shall be telling this with a sigh
Somewhere ages and ages hence:
Two roads diverged in a wood, and I—
I took the one less travelled by,
And that has made all the difference.

Robert Frost

There is a single light of science, and to brighten it
anywhere is to brighten it everywhere.

Issac Asimov
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Abstract

Laser scribing of thin glass has proven problematic due to inefficient optical absorption and difficulty achieving economical processing speeds while maintaining edge quality. Laser processing of glass is pertinent to touch screen, display, microfluidic, microoptic and photovoltaic applications. At thicknesses <100μm glass benefits from added flexible functionality. In addition to high optical transparency, electrical insulation and good chemical resistance, thin glass is a preferable material choice for many applications. Thin flexible glass offers an opportunity to substitute sheet-fed with reel-to-reel processing, reducing processing time and material handling issues. Unique absorption and thermalisation mechanisms associated with ultrashort pulse ablation have opened new opportunities for laser material processing, especially for optically transparent materials such as glass. A robust and reconfigurable thin flexible glass cutting technique, compatible with reel-to-reel manufacturing, has yet to be established.

Initially this work benchmarks laser ablative processing of glass. Laser sources including a CO₂ laser, short pulse UV laser and an ultrashort pulse IR laser, are used. The contrasting absorption and material removal mechanisms produce diverse processing results. It was concluded that ultrashort pulse lasers are the most suitable for full body ablative processing of thin glass, due to precise non-linear absorption mechanisms and minimal thermal effects. Cross sections of glass which were scribed with a P polarised laser (relative to the trench wall) showed damage regions extending away from the trench walls, and correlated damage on the rear surface. This is indicative of damage caused by light transmission through the walls of the trench. The damage was reduced by rotating the polarisation to S polarised, due to the increased reflectance from the trench walls. It was found that S polarised light also required less passes to ablate through the glass substrate. A processing window capturing the peak of the polarisation effect was identified. An optical model was developed to predict the effect of polarisation on the intensity distribution reaching the rear surface of the glass. The model showed that S polarised light confined a greater amount of light in the trench. Consequently we see an increased fluence incident on the central region of the trench. Even
with precise control of parameters, laser processing of thin glass speed is an order of magnitude below the required level.

An alternative laser scribing method, which utilises surface stress raisers to enable controlled mechanical fracture of glass, was developed. An ultrashort laser source is used to precisely pattern elliptical recesses on the sample surface. The apex of an ellipse concentrates tensile stresses in a brittle material. Depending elliptical dimensions the stress concentration factor can be several tens in magnitude. A beam delivery system was designed to produce a focused elliptical spot. When scanned, the system generates a plurality of separated aligned elliptical recesses across the glass surface. The orientation of the ellipses defines a preferred scribing path. Tensile stress can be applied orthogonally to the path to cause mode I fracture. The quality of the right angular cuts in thin flexible glass, processed with this method, are of higher quality and strength than are possible with a full body laser cut. Curved scribed are possible with this technique by rotating the cylindrical lens along an arc while the laser is scanned in a curved path. The stress field around a stress raiser was analysed using the FEM. A non-contact method for fracturing scribed brittle substrates was developed. The process uses compressed-air jets, controlled by high-speed valves, to produce mechanical resonance and induce a bending stress in the glass substrate. If the stress is sufficient the substrate will fracture along the scribed line. The resonant frequency of the beam was studied analytically by modelling the substrate as a beam with both ends fixed. FEM analysis on the beam was also performed to compare with the analytical results.

The optical setup for the mechanically inspired scribing process is simple, low cost and compatible with reel-to-reel manufacturing platforms. Consequently the stress raiser process, together with the resonant fracture technique, offers an alternative to other processes which employ high numerical aperture optics for thin glass scribing.
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I have been fortunate in my career so far to have surrounded by many brilliant people. This thesis would not have been possible without their support. Here I would like to acknowledge their contributions.

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Thanks to the Smokies crew for providing a welcome daily distraction and an opportunity to discuss the finer things in life. I wish you all the best for the futures.

Finally I must thank Olivia for supporting and encouraging me throughout this long journey.
Declaration

The work in this thesis is based on the research carried out at the National Centre for Laser Applications (NCLA), School of Physics, National University of Ireland Galway. I, Adam Collins, hereby certify that this thesis has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a degree or qualification.
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Chapter 1
Introduction

It is indicative of the influence of lasers in modern technology that the acronym LASER has become an accepted noun in the Oxford English dictionary. Lasers are a unique sources of electromagnetic radiation emitting light with high spatial coherence, monochromaticity and high temporal resolution. Lasers provide a precise, quick, sterile, reconfigurable and non-contact solution for material processing. New processing methods are possible that are not feasible with standard techniques. Stimulated emission of light in the infrared and optical region was first theorised by Schawlow and Townes in 1958 [1]. The ideal laser gain medium was debated, with difficulty determining a material which could provide sufficient gain. Maiman [2] first demonstrated lasing two years later, using a synthetic ruby rod gain medium pumped by a flash lamp. The ends of the rod were silvered to achieve oscillation. In the decades since this first demonstration laser technology has become widely adopted in a variety of scientific, industrial and consumer applications. The range of applications of lasers continues to increase as the technology becomes more mature, accurate and economical.

This thesis investigates the use of lasers for the scribing of silica based glass materials. Glass is an important material which has been used by humans for millennia. Glass is an amorphous brittle material which is typically transparent to visible wavelengths. The most common type of glass is silica (silicon dioxide) glass. Silicon and oxygen are the two most abundant elements in the earth’s crust [3] providing ample and accessible raw materials for glass production. Glass has a good chemical resistance, high optical transparency, electrical insulation and moderate flexibility for thicknesses below 100µm. For this reason glass is suitable for many applications such as laboratory glassware, optical elements, lighting, telecommunications and optoelectronic devices.

The first man-made glasses were used by the ancient Egyptians as decorative beads and cutting tools, dating from at least 7000 B.C. [4]. Today glass has an array of applications. In recent history glass has been a key component of major technological advances. Glass vacuum tubes were ubiquitous in all manner of technologies during the digital revolution in the early
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twentieth century. More recently glass optical fibres revolutionised telecommunication, triggering an era of low cost and high bandwidth communication, referred to as the information age. Glass is erroneously thought of as a weak and inflexible material. Major international corporations (Corning, Nippon Electric Glass, Schott) devote enormous resources developing new functionalities for glass. Thin glass based flexible large area electronics may trigger a ‘glass age’ as advertised by Corning’s ‘a day made of glass’ presentation[5]. Corning market a vision of the near future where flexible smart displays have been incorporated into nearly every part of life. While this may be somewhat idealistic, the surge in demand for consumer electronics over the past decade indicates an overwhelmingly positive response to touch screen smart displays.

1.1 Motivation

Glass is a pervasive material; it is used ubiquitously in consumer products and in industrial environments. Global mega trends in areas such as energy harvesting, urbanisation, mobility, smart technology and advanced materials has seen a growth in interest in thin flexible and printable electronics. Practical examples include organic LEDs, photovoltaics, touch sensitive screens, smart windows and sensors. The common denominator across these trends is the substrate used: thin flexible glass. Glass has favourable optical and mechanical properties as well as good chemical resistance. This makes glass a suitable substrate choice for a range of applications. Glass manufacturers are continuously refining manufacturing techniques to deliver larger and thinner glass sheets to meet consumer electronics demands. At the time of writing manufacturers offer generation 10 display glass with dimensions of 2800x3100x0.7mm and generation 5 ultrathin glasses with dimensions of 0.5x0.5x0.025mm[6, 7], a fraction of the thickness of a human hair.

Glass benefits from added flexible functionality at such thicknesses. Ultrathin glass can be wound in a spool and offers an opportunity to substitute sheet-to-sheet processing with a reel-to-reel process. A reel-to-reel platform is a manufacturing tool for carrying out additive and subtractive processing on continuously rolling, flexible substrates. Reel-to-reel processing reduces processing time and material handling issues, thus reducing manufacturing costs [8, 9]. Typical processes for large area electronics manufacture include spraying and curing of metal and transparent conductive films, laser patterning of films and singulation of parts.
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(Figure 1.1). This process allows a larger area to be processed at a higher speed, compared with standard photolithography techniques on silicon.

![Figure 1.1: Illustration of typical reel-to-reel machine for large area electronics manufacture. Other steps such as cleaning and inspection are not shown here.](image)

Most aspects of the reel-to-reel process chain for thin glass processing are well developed with a high technology readiness level [10]. Transportation and handling of glass spools had proven problematic. Bonding of glass to a polymer carrier layer has reduced these issues. Glass cutting and part singulation remains a challenging issue. Reconfigurable, zero width, debris free, high speed separation of shaped materials is a key technical challenge throughout manufacturing. Traditional cutting tools (diamond scribing tools, carbide cutting wheels) are mechanical in nature and lack the adaptability necessary for reel-to-reel production. Laser based melt and blow or ablative processes provide the required versatility but are uneconomical. Efficient energy coupling into transparent substrates, such as glass, is an issue for some lasers. Thermalisation of the absorbed energy in the material is complex and proceeds along many diverse pathways. The precision of laser processing is limited by a typically micron scale heat affected zone as well as micro-cracking at the cut edge due to the build-up of thermal stress. For high aspect ratio cuts the extraction of debris from the cut is a challenge.

Other substrate choices for flexible large area electronic manufacturing include polymers, such as polyimide (PI), or thin metal foils, such as stainless steel. Laser cutting processes for these materials are more robust. PI is lightweight and strong however it has poor chemical resistance and a low melting temperature and so is unsuitable for the heat treatments
required in organic LED manufacture. Metallic foil substrates are low cost with good thermal and chemical properties; however they are typically opaque to visible wavelengths and have high surface roughness and high mass. Due to these fundamental drawbacks thin glass is the most suitable substrate for flexible large area electronic manufacturing, despite challenges in cutting and handling of brittle substrates.

1.2 Opportunity

The advent of chirped pulse amplification [11] facilitated the amplification of ultrashort laser pulses, without adverse effects. The peak intensity of lasers has increased enormously since. Intensities of $10^{20}$W/cm$^2$ are available from desktop lasers, these kinds of intensities are sufficient to produce ions with MeV energies and strong accelerations of $10^{21}$ times earth's gravity. Ultrashort lasers incident on a transparent material will experience a range of nonlinear optical effects and will cause nonlinear photoionisation and ablation in the material, depending on the intensity. The extremely short pulse duration results in a negligible heat affected zone around the ablated region. Authors [12, 13] have demonstrated high quality features and cuts in glass produced using ultrashort lasers. Consequently ultrashort lasers may offer a solution to part singulation in a reel-to-reel glass based process. The dynamics of the absorption and material removal processes are a debated issue. Real time characterisation of the dynamic absorption mechanisms is difficult due to the short timescales involved. This project provides an opportunity to investigate such phenomena in an area which is industrially relevant.

Multinational laser manufacturers are in constant competition to improve laser performance. Consequently the capabilities of ultrashort lasers are increasing while the cost of ownership falls. State of the art ultrashort laser products offer 400W of average power, with high repetition rates of 2MHz [14]. Some manufacturers offer tunable wavelengths lasers which could be adjusted depending on the material properties. CNC beam scanning systems are available to complement the high repetition rate of the laser. Precise positioning of the sample in the laser focus can be achieved with micro-positioning translation stages. Ultrashort lasers are becoming more reliable as the technology matures. The reduction in size, complexity and cost is crucial for ultrashort lasers to become practical for industry. Ultrashort lasers may offer a viable solution for thin glass cutting issues.
This project is set at the interface of a multibillion dollar value chain process, lacking a key processing step, and a rapidly improving laser technology with potential to provide a solution.

1.3 Objectives

The aim of this study is to investigate the interaction of laser pulses with dielectric substrates, in particular ultrashort laser pulses. Lasers have a wide array of adjustable parameters, the impact of some of these parameters on the laser interaction will be investigated. Techniques to maximise coupling of laser energy into dielectric substrates will be identified. These techniques will be applied to develop laser glass scribing processes for future advanced reel-to-reel manufacturing applications. Novel processing techniques will also be considered. The objectives may be summarised as follows:

- Investigate the effect of laser parameters on energy coupling in dielectrics, material removal rates and feature quality.
- Develop novel processes for glass scribing and cleaving.
- Develop computational simulations to better understand pertinent phenomena.
- Analyse results and demonstrate an industrially practical process.

1.4 Synopsis

This thesis is comprised of seven chapters, including the current chapter. A brief synopsis of each chapter is given below.

Chapter 1 introduces the subject and motivation of the research.

Chapter 2 describes the theory behind the main subject areas of the thesis: laser technology, laser material interaction and fracture mechanics. The current state of the art for glass processing with lasers or otherwise is also reviewed.

Chapter 3 lists equipment and experimental techniques used in the experimental sections. Laser processing and characterisation equipment and techniques are discussed.
Chapter 4 benchmarks traditional full body laser cutting for glass. A variety of laser sources were used to process glass with different settings for laser power, overlap, polarisation and spot size. Transmission through the sample was measured experimentally. The transmission data was used to develop an optical ray tracing model which provided an explanation for some phenomena seen in the glass after laser processing.

Chapter 5 considers a novel, mechanically inspired, method for inducing controlled fracture in glass. A beam delivery system is designed using optical design software to focus the laser to an elliptical spot shape. This spot is used to produce rows of aligned elliptical recesses in the glass surface. The recesses amplify tensile stresses in the material and define a plane of preferred cleavage. Methods for applying tensile stress to the substrate are discussed.

Chapter 6 introduces a resonance fracture method for fracturing samples produced using the mechanically inspired process described in chapter 5. Analytic and computational predictions of the resonant frequency and mode shape of the glass substrate are determined. A mechanical resonance setup, which uses periodic jets of compressed air, is designed and applied to the glass fracture process. A high speed camera is used to monitor oscillations.

Chapter 7 evaluates the chief results of the thesis against the initial objectives and discusses opportunities for further development.

1.5 Publications and Patents


### 1.6 Conference Presentations


Chapter 2
Theoretical Background and Literature Review

This chapter will provide an introduction to the theory and relevant literature necessary to interpret results presented in subsequent chapters. This literature review deals with the propagation of light, laser physics, interaction of laser pulses with transparent substrates and brittle fracture theory.

Models for describing linear and nonlinear optical effects are presented. The production of short and ultrashort pulses will be described followed by the nonlinear absorption mechanisms which couple ultrashort pulses into dielectric substrates. Particular attention will be paid to the advantages and disadvantages of ultrashort pulses compared with short pulse lasers. The review of fracture mechanics will discuss the role of stress raisers in the fracture of brittle materials and the stress concentration factor around a crack tip. The thermodynamic approach to fracture prediction will be discussed along with dynamical crack propagation effects which occur at terminal crack velocity.

2.1 Propagation of Light in Glass

A beam of light incident on a substrate will undergo reflection, refraction and absorption. The amount of each is dependent on the material and light properties. Glass is an amorphous insulator. Like all insulators glass has a transparency range. The unique feature of glass is that the transparency range typically covers the entire visible range. Pure fused silica glass has a transparency range from 200nm to >2000nm[15]. The UV fundamental absorption edge is abrupt (see Figure 3.2) and is due to electronic excitations in the material. The IR absorption edge is more gradual and is due to the increasing coupling of light with vibrational modes in the material. Optical absorption models and other optical effects are discussed. Theory in this section is adapted predominantly from Fox[15] and Hecht[16].
The work of Maxwell and others since has shown that light propagates as a wave with an electric and magnetic component. Light exhibits wave phenomena such as interference, diffraction and reflection. Combining the four Maxwell equations we can describe the propagation of an electromagnetic wave inside a homogeneous dielectric medium with the electromagnetic wave equation (1).

\[ \nabla^2 E = \mu_0 \mu_r \varepsilon_0 \varepsilon_r \frac{d^2 E}{dt^2} \]  

The modern view of quantum electrodynamics finds light propagates as a series of massless, energetic particles known as photons. Both approaches are necessary to interpret the propagation of light through a material.

### 2.1.1 Chromatic Dispersion

The presence of a dielectric medium in a region of free space will alter the permittivity (\(\varepsilon\)) and permeability (\(\mu\)) of the region. The net effect is a reduction in the phase speed (\(v\)) of an electromagnetic wave in the medium. The ratio of the phase speed in a vacuum to that in the particular medium is referred to as the refractive index (\(n\)). The refractive index of all materials varies with wavelength. This phenomenon is known as chromatic dispersion.

\[ n = \frac{c}{v} = \sqrt{\frac{\varepsilon \mu}{\varepsilon_0 \mu_0}} \]  

A simple and effective model for understanding some of the optical properties of glass is the classical Lorentz dipole oscillator model. This model deals with the interactions on an atomic level. The oscillating electric field of the incident light will perturb the bound electron cloud of the atom. The electrons will experience a restoring force back to their equilibrium position. This interaction can be modelled as a damped harmonic oscillator. The resonant frequency (\(\omega_0\)) depends on the spring constant of the restoring force (\(K\)) and the reduced mass of the electron and nucleus (\(\mu\)): \(\omega_0 = \sqrt{K/\mu}\). Ignoring the motion of the nucleus we can write an equation of motion for the electron (3). We have displacement \(x\), damping \(\gamma\), electron mass \(m_e\), electron charge \(e\) and the applied electric field \(E(t)\).

\[ m_e \frac{d^2 x}{dt^2} + m_e \gamma \frac{dx}{dt} + m_e \omega_0^2 x = -eE(t) \]  

Considering the phase and amplitude for the electric field we can determine the amplitude of the electron displacement. Assuming the electron oscillation frequency is the
same as \( E(t) \) and that \( d^2x/dt^2 \) is similar in form to \( x \) we can solve (3) for the amplitude of the electron displacement \( (X_0) \) (4).

\[
X_0 = -\frac{eE_0/m_0}{\omega_0^2 - \omega^2 + i\gamma \omega}
\]  

(4)

The displacement will give rise to dipole moments which will contribute an additional field component, referred to as the electric polarisation. The dependence of the permittivity of a medium on the optical frequency is due to electric polarisation mechanisms at a particular frequency. If we have \( N \) atoms per unit volume the resonant contribution to the overall polarisation \( (P_{\text{resonant}}) \) can be written as (5).

\[
P_{\text{resonant}} = \frac{Ne^2}{m_0} \frac{1}{\omega_0^2 - \omega^2 + i\gamma \omega}
\]  

(5)

Given that the electric displacement \( (D) \) is related to the polarisation by \( D=\varepsilon_0E+P_{\text{background}}+P_{\text{resonant}} \) and for isotropic materials \( D=\varepsilon_0\varepsilon E \), we can derive an expression for the dielectric constant (6). \( P_{\text{background}} \) accounts for non-resonant background polarisation in the material. We sum to \( j \) to account for \( j \) resonances in the material. The refractive index is related to the dielectric constant, in a transparent medium, by \( n=\sqrt{\varepsilon} \).

\[
\varepsilon_r(\omega) = 1 + \frac{Ne^2}{\varepsilon_0 m_e} \sum \frac{1}{\omega_j^2 - \omega^2 + i\gamma_j \omega}
\]  

(6)

This expression is plotted against measured values of \( n \) for fused silica in Figure 2.1. The technique used for determining the refractive index depends on the wavelength, and include the minimum deviation angle method, interferometric methods and the Kramers-Krönig analysis of reflectance data[17]. The dipole oscillator model matches the general features of the measured values. The variation of absorption strength between differing atomic transitions cannot be explained using this model and requires quantum treatment. An empirically derived oscillator strength term \( (f_j) \) can be applied to each transition to account for this.
Theoretical Background and Literature Review

Figure 2.1: Plot of experimental measurements of refractive index of SiO$_2$, from Palik[17], and the dipole oscillator model expression (6) with resonances at 0.12µm, 8.9µm and 21µm. The resonances correspond to electronic transitions at short wavelengths and vibrational bands at long wavelengths.

The non-resonant background polarisation can be expressed in terms of the linear susceptibility tensor ($\chi$).

$$P_{\text{background}} = \varepsilon_0 \chi E$$  \hspace{1cm} (7)

2.1.2 Vibrational Interaction

Bound atoms in a solid will experience a restoring force if displaced from their equilibrium position. This causes a vibration at a characteristic frequency. For a crystalline material these frequencies are known as phonon modes. In an amorphous material, such as glass, atoms will vibrate in delocalised phonon modes. Resonant phonon frequencies occur in the IR region and so can interact directly with light. A photon couples to the phonon modes of an atom through its oscillating electric field. For perturbation by the electric field to occur the atom must have some electric charge. This limits optically active phonon modes to materials with ionic bonding character. For covalently bonded materials, such as silicon, we have no IR active phonon modes however other phonon modes exist.

The electric field associated with light is a transverse wave and so will excite transverse vibrational modes in the atom. The material excitation can be modelled by applying the
classical oscillator model. We consider the equations of motion for the perturbed atoms (8) with a damping term ($\gamma$). $x$ is the relative displacement of the positive and negative ions, $q$ is the ionic charge, $\mu$ is the reduced mass, $E(t)$ is the external electric field and $\nu$ is the resonant frequency of the phonon mode.

\[
\frac{d^2x}{dt^2} + \gamma \frac{dx}{dt} + \nu^2 x = \frac{q}{\mu} E(t)
\]

(8)

This expression is identical in form to the Lorentz dipole oscillator model, discussed in section 2.1.1, which describes the vibration of bound electrons. Consequently we can borrow the formula for the frequency dependence of the dielectric constant (9). In this case $\chi$ is the non-resonant nonlinear susceptibility of the material.

\[
\varepsilon_r(\omega) = 1 + \chi + \frac{Nq^2}{\varepsilon_0\mu} \frac{1}{\nu^2 - \omega^2 + i\gamma\omega}
\]

(9)

This expression accurately predicts the dielectric constant for most semiconductors. High absorption coefficients (~10^7 cm⁻¹) are seen whenever the optical frequency matches the natural resonances of the material. The absorption coefficient is so high it is often difficult to measure experimentally, and requires very thin samples to get an appreciable transmission signal.

### 2.1.3 Electronic Interaction

Isolated atoms have discrete electron energy states, however atoms in a solid form energy bands due to delocalised states. Silica has a well-defined fundamental absorption edge in the UV spectral range. This absorption band occurs due optical excitation of electrons across the material bandgap. Pure fused silica has a 10eV material bandgap [15] requiring 123nm wavelength photons to excite electrons across this gap. Interband transitions are observed in all materials. The oscillator model struggles to account for continuous absorption bands. This behaviour is best understood using quantum mechanical treatment. Equation (10) is formulated by applying the law of conservation of energy to the electronic excitation, by a photon with energy $h\omega$, from the initial energy $E_i$ across the bandgap to final energy $E_f$. For excitation to occur the photon energy must be greater than material bandgap ($h\omega>E_g$). There are a continuous range of energy states available in the conduction band making interband transitions possible over a continuous range of energies. Selection rules also apply; there must be an
available electron in the valence band and, according to the Pauli exclusion principle, an empty state in the conduction band.

\[ E_f = E_i + \hbar \omega \]  

(10)

Absorption rates can be understood by studying the band structure of silica and applying a quantum mechanical treatment. A transition rate \( W_{i-f} \) can be defined in accordance with Fermi’s golden rule. The transition rate is dependent on the matrix element \( M \) describing electron perturbation and the density of states \( g(\hbar \omega) \)

\[ W_{i-f} = \frac{2\pi}{\hbar} |M| g(\hbar \omega) \]  

(11)

To estimate the matrix element a semi-classical approach is adopted where the light is considered a wave but the electrons are treated quantum mechanically. The matrix element can be written in integral form where \( H' \) is the perturbation associated with the light wave, \( r \) is the position vector of the electron and \( \psi_i \) and \( \psi_f \) are wavefunctions.

\[ M = \int \psi_f(r) H'(r) \psi_i(r) d^3r \]  

(12)

Light is a plane wave so the perturbation of a light wave can be written as a product of a plane wave with wave vector \( k \). Electronic states in a crystal lattice are described by periodic Bloch functions. This allows us to write the wavefunctions as a product of a plane wave and a periodic envelope functions \( u \) with a period equal to the lattice constant.

\[ M = \frac{e}{V} \int u_f(r) e^{-ik_{f} \cdot r} (E_0 \cdot r e^{ik \cdot r}) u_i(r) e^{ik \cdot r} d^3r \]  

(13)

Due to conservation of momentum any change in crystal momentum of the electron must equal the momentum of the photon. Rather than integrate over the entire crystal we can sum individual unit cells (14). This expression allows us to calculate the probability of electric-dipole transitions. Determining the character of the bands involved requires group theory.

\[ M \propto \int_{unit\ cell} u_i(r) x u_f(r) d^3r \]  

(14)

The joint density of states describes \( g(E) \) the distribution of energy states in the continuous bands. For electrons in a parabolic band with effective mass \( m^* \) the density of states is given by (15).

\[ g(E) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E} \]  

(15)
Considering a direct transition ($k=0$) with $E_g \geq \hbar \omega$ the density of states is given by (16). For $E_g < \hbar \omega$ the density of states is zero.

\[ g(\hbar \omega) = \frac{1}{2 \pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{\hbar \omega - E_g} \]  

Consequently we expect a $\sqrt{(\hbar \omega - E_g)}$ relationship between the absorption coefficient and the optical frequency. This relationship holds for most direct bandgap semiconductors. When an external electric field is applied the absorption coefficient for photons with energy less than the bandgap is no longer zero. The absorption coefficient decreases exponentially with $(E_g - \hbar \omega)$. This is known as the Frans-Keldysh effect.

### 2.1.4 Non-linear Interaction

For intense light (e.g. from a laser source) the linear equation (7) is no longer valid. We enter a nonlinear regime, analogous to overloading a spring into a nonlinear response. We can express the nonlinear dependence of the material polarisation on the applied electric field by expanding the linear equation as a power series (17). $\chi^n$ is the nth order nonlinear susceptibility.

\[ P_{\text{nonlinear}} = \varepsilon_0 [\chi^1 E + \chi^2 EE + \chi^3 EEE ... ] = P_1 + P_2 + P_3 ... \]  

Recalling that $\varepsilon = 1 + \chi$ we see that the dielectric constant, and therefore the refractive index, has a dependence on the electric field due to the nonlinear susceptibilities. This leads to a range of nonlinear phenomena. Most of these are attributed to the $\chi^2$ or $\chi^3$ terms, as higher terms become insignificantly small. $\chi$ is typically much larger than $\chi^2$ and $\chi^3$. Consequently the higher order terms are negligible at lower light intensities. Nonlinear effects become apparent when the electric field of the light is comparable to the electronic binding force between an electron and a nucleus, typically around 0.5TVm$^{-1}$. Optical intensities of the order of $10^{19}$Wm$^{-2}$ are required to produce such electric fields. Each of the electric fields on the right hand side of equation (17) can have different frequency components. The resulting nonlinear polarisation wave will oscillate at a frequency equal to the sum or difference of these frequencies. The origin of the optical nonlinearities depends on the optical frequency of the light and whether it is close to the transition frequency of the atoms.

In the case where the photon has sufficient energy to excite an electron across the bandgap we have a non-negligible amount of stimulated emission occurring for high intensity light. The net effect is a reduction in the absorption coefficient. A saturation intensity ($I_s$) can
be defined to account for this. The absorption coefficient has a linear dependence on intensity and, thus, an $E^2$ dependence on the electric field.

$$\alpha(I) = \alpha_0 - \frac{\alpha_0 I}{I_0}$$  \hspace{1cm} (18)

For photons with energy less the material bandgap the strong electric field will cause large electron displacements, resulting in a nonlinear restoring force. Considering again the dipole oscillator model from section 2.1.1, we can account for this large displacement by applying a similar analysis as before, but with an anharmonic oscillator term ($C_3$). Using this approach an expression for the second order nonlinear susceptibility can be derived (19).

$$\chi^2 = m_0 C_3 \chi(\omega)^2 \chi(2\omega) \epsilon_0^2$$  \hspace{1cm} (19)

The significant result in (19) is that when $\chi^2$ is nonzero the medium generates a wave with a frequency of $2\omega$ when driven at a frequency $\omega$. This effect is used for conversion of laser wavelengths. A complete list of second order nonlinear effects is given in Table 2.1. Applying a DC electric field to an optical material can cause a variation in the refractive index, referred to as the Pockels effect. This can be considered a second–order nonlinearity in which the frequency of the driving field is zero. This effect is used in Pockels cells to induce birefringence in a crystal. The reciprocal of this effect occurs when polarised light causes a constant electric polarisation in the material. This results in a voltage proportional to the electric field of the light and is known as optical rectification. Sum and difference frequency mixing are similar to the frequency doubling effect. Two pump beams with a different frequency are applied to the medium and the output is the sum or difference of the frequencies of the pump beams. Down conversion is the inverse of the sum frequency mixing process.

Table 2.1: Second order nonlinear effects. $\omega$ is the optical frequency. A frequency of 0 corresponds to a stationary field (i.e. DC).

<table>
<thead>
<tr>
<th>Effect</th>
<th>Input Frequency</th>
<th>Output Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency Doubling</td>
<td>$\omega$</td>
<td>$2\omega$</td>
</tr>
<tr>
<td>Optical Rectification</td>
<td>$\omega$</td>
<td>0</td>
</tr>
<tr>
<td>Down Conversion</td>
<td>$\omega$</td>
<td>$\omega_1, \omega_2$</td>
</tr>
<tr>
<td>Sum Frequency Mixing</td>
<td>$\omega_1, \omega_2$</td>
<td>$(\omega_1 + \omega_2)$</td>
</tr>
<tr>
<td>Difference Frequency Mixing</td>
<td>$\omega_1, \omega_2$</td>
<td>$</td>
</tr>
<tr>
<td>Pockels Effect</td>
<td>$\omega, 0$</td>
<td>$\omega$</td>
</tr>
</tbody>
</table>
Third order effects are dominant in isotropic materials such as glass. In isotropic materials the atomic structure possesses inversion symmetry causing the even powers in (17) to vanish. If we reverse the direction of the electric field even order nonlinear polarisation terms are unchanged: \( P_2(-E) = P_2(E) \). Neumann’s principle states that if a crystal has inversion symmetry its physical properties must be invariant with respect to the same symmetry operations. In terms of the same coordinate system in an inverted crystal all components of \( P_2 \) will change sign. To satisfy Neumann’s principle, in this case, \( \chi^2 \) must vanish. Therefore any material with inversion symmetry in its atomic structure will not experience even order nonlinear effects.

The third order susceptibility is therefore the highest nonzero nonlinear susceptibility for materials with inversion symmetry. Third order effects occur when three input electric fields are applied to the medium. A frequency tripling process will occur analogous to the frequency doubling process. Three input waves at the same frequency will result in an output wave with triple the frequency. Again precise phase matching is required for efficient conversion. Practically it is simpler to produce a frequency tripled beam through two frequency doubling processes rather than by a single frequency tripling process, as \( \chi^3 \) is small.

Incident light with one frequency incident on the nonlinear medium will produce a third order polarisation wave at the same frequency. This is known as the optical Kerr effect. There are no phase matching requirements in this case as the nonlinear photoionisation is at the same frequency as the driving wave and so the fields are in phase at any point in the medium. Recalling that \( \varepsilon_r = \varepsilon_0 + \chi \) and comparing this with equation (17) with \( \chi^2 = 0 \) the nonlinear dielectric constant can be written as (20). The intensity is related to the electric field by \( I = c\varepsilon_0(n_0^2\varepsilon_r)E^2/2 \).

\[
\varepsilon_r^{\text{nonlinear}} = 1 + \chi^1 + \chi^3 E^2 = \varepsilon_r + \frac{2\chi^3 I}{c\varepsilon_0\sqrt{\varepsilon_r}} \tag{20}
\]

Higher order susceptibilities have been neglected in this case. The refractive index is given by the square root of the relative dielectric constant. Therefore the refractive index is dependent on the applied electric field. For the case where \( \varepsilon_r >> \chi^2 E^2 \) the relationship is given by (21). The linear part of the refractive index is written as \( n_0 = \sqrt{\varepsilon_r} \) and the nonlinear part \( n_2 = \chi^3/(n_0^2 c \varepsilon_0) \)

\[
\sqrt{\varepsilon_r^{\text{nonlinear}}} = \sqrt{\varepsilon_r + \frac{2\chi^3 I}{c\varepsilon_0\sqrt{\varepsilon_r}}} = n_0 + \frac{\chi^3}{n_0^2 c \varepsilon_0} I = n_0 + n_2 I \tag{21}
\]
The non-linear refractive index \(n_2\) is directly proportional to \(\chi^{(3)}\) and varies with applied intensity. \(n_2\) is typically negative for short wavelengths and positive for long wavelengths. In laser applications this leads to two important effects, namely self-focusing and self-phase modulation. Self-focusing occurs due to the Gaussian intensity distribution of a laser beam. The outer parts of the beam will have a lower intensity, and therefore a lower refractive index, than the central part. This causes the material to act as a positive lens focusing the light. Self-phase modulation is the temporal analogy of self-focusing. A laser pulse has Gaussian intensity distribution temporally causing a refractive index variation over the course of the pulse. This leads to a variation in the phase of the beam. For photons with energy equal or greater to the material bandgap an absorption intensity dependence is observed similar to (18).

### 2.2 Short and Ultrashort Laser Pulse Generation

Theory and methods for generation of laser pulses will be examined in this section. Laser theory in this section has been adapted predominately from Siegman [18]. The elements common to all lasers are the laser gain medium, a method of pumping this medium and optical feedback elements to allow the beam to make a prescribed number of passes through the laser medium. In the ultrashort laser case, a temporal pulse stretcher and compressor are required to prevent beam distortion, and possibly damage to the gain medium, due to the high laser intensities.

There is an almost limitless number of possible laser devices given the variety of laser mediums and laser pumping methods. Each device has particular advantages and disadvantages. The choice of laser device depends on the application. All lasers are monochromatic and collimated, some more so than others. Some lasers are widely tuneable and are used for spectroscopic applications. Some lasers are very frequency stable and can be used as a temporal standard. CO\(_2\) have been demonstrated operating at 70% efficiency while optically pumped solid state lasers typically achieve ~2% efficiency. For material processing a high peak power and short pulse duration is required which necessitates a broadband spectral emission from the laser transition.
2.2.1 Laser Medium

Lasing is achieved through stimulated emission from a suitable excited gain medium. Stimulated emission occurs when a photon interacts with an excited electron resulting in the emission of an additional photon. The emitting atom acts similar to a miniature resonant antenna. The oscillation of the electron is driven by the incident photon. Consequently the emitted photon will have identical phase, frequency, polarisation and direction as the incident photon.

The gain medium must have a three or more energy level band structure to sustain the population inversion necessary for lasing to occur. Considering a simple three energy level system \((E_0, E_1, E_2)\), electrons are excited to the highest energy level \((E_2)\) by the pumping process. Spontaneous decay to energy level \(E_1\) will occur through radiative or non-radiative processes. Non-radiative processes include heating of the surrounding material. The electrons in \(E_1\) can relax back to the ground state \(E_0\) only through spontaneous and stimulated emission of photons. Population inversion can be achieved if the rate of relaxation from \(E_1\) to \(E_0\) \((\gamma_{10})\) is lower than for \(E_2\) to \(E_1\) \((\gamma_{21})\). Electrons will accumulate in the \(E_1\) energy level. If at least half of the electrons are pumped from \(E_0\) to \(E_2\) a population inversion between \(E_1\) and \(E_0\) can be achieved. Once a population inversion has occurred, a photon with the correct energy will release an additional and identical photon as it passes through the medium. Figure 2.2 shows three and four level atomic energy level systems which have achieved population inversion. A three level system is impractical as very strong pumping is required to maintain the population inversion. At least half of the electron population must be excited to energy level \(E_2\), making the process inefficient. Four or more energy level systems are more efficient. Population inversion can be achieved by pumping only a small amount of electrons to energy level \(E_3\) as long as the relaxation rate \(\gamma_{21}\) is lower than \(\gamma_{32}\) and \(\gamma_{10}\). Radiative emissions from transitions other than the desired laser transition will add a small amount of noise to the signal. This noise is negligible, unless the pumping rate is low.
Figure 2.2: Three level and four level energy system population diagram. The three level system (left) has been pumped to achieve population inversion between levels \(E_1\) and \(E_0\). This is possible as the transition rate \(\gamma_{10} < \gamma_{21}\). The four level system (right) has been pumped to achieve population inversion between levels \(E_2\) and \(E_1\). This is possible as the transition rate \(\gamma_{21} < \gamma_{32}, \gamma_{10}\). The magnitude of the population inversion depends on the pumping rate \(R_p\).

Laser media are not limited to solids. Helium neon gas is used as a laser medium for consumer electronics applications due to their low cost and ease of operation. Long wavelength CO\(_2\) lasers are available as well as short wavelength excimer lasers (e.g. KrF). Gas laser media are typically pumped by a DC current or an applied RF frequency. The energy level picture is analogous to Figure 2.2, however vibrational modes are excited in the molecules rather than electronic modes. Regardless of the laser medium the wavelength \((\lambda)\) of the emitted photon is determined by the difference in energy levels \((E_1, E_2)\) by Planck’s law (22).

\[
\lambda = \frac{hc}{E_2 - E_1}
\]  

(22)

2.2.2 Laser Oscillator

A laser oscillator consists of a laser medium and pumping source placed inside an optical feedback mechanism. Typically the feedback mechanism is two aligned end mirrors similar to a Fabry-Pérot interferometer. End mirrors in oscillators are curved to reduce diffraction and dispersion effects. Initially the excited medium will spontaneously emit photons in all directions. Photons which are parallel to the optical axis will be trapped and make multiple passes around the oscillator. For net amplification to occur the amplification for each round
trip in the oscillator must exceed losses. The gain coefficient defines the gain per unit length when a photon with the relevant wavelength propagates through the excited laser cavity. Equation (23) shows an expression for the gain coefficient \( \gamma(\omega) \) when the photon flux is small and the material is far from saturation. \((N_2-N_1)\) is the population density difference, \(\sigma(\omega)\) is the transition cross section, \(t_{sp}\) is the spontaneous lifetime of an excited electron in the upper energy level, \(\lambda\) is the laser wavelength and \(g(\omega)\) is the transition lineshape. \((N_2-N_1)\) increases with the pumping rate.

\[
\gamma(\omega) = [N_2 - N_1] \sigma(\omega) = [N_2 - N_1] \frac{\lambda^2}{8\pi t_{sp}} g(\omega)
\]  \hspace{1cm} (23)

Losses include reflection losses at the mirrors and scattering. Equation (24) shows an expression for the loss per round trip in the laser cavity. \(\alpha_s\) is the attenuation coefficient accounting for absorption and scattering losses. \(R_1\) and \(R_2\) are the reflectivity of the cavity end mirrors and \(L\) is the cavity length. \(\alpha_r\) represents the total attenuation per unit length.

\[
R_1 R_2 \exp(-2\alpha_s L) = \exp(-2\alpha_r L)
\]  \hspace{1cm} (24)

For net amplification to occur in the laser cavity the condition \(\gamma(\omega) > \alpha_r\) must be satisfied. Using equations (23) and (24) we can rewrite this condition \(N_0 > N_t\). \(N_t\) is the threshold population difference given by \(N_t = \alpha_r / \sigma(\omega) = 1/c\tau_{\text{photon}}\sigma(\omega)\) where \(\tau_{\text{photon}}\) is the photon lifetime. Inserting the expression for the transition cross section \(\sigma(\omega)\) we can derive an expression for the threshold population difference in terms of wavelength and photon lifetime (23). It is clear from this expression that achieving laser oscillation becomes increasingly challenging with decreasing wavelength.

\[
N_t = \frac{8\pi t_{sp}}{\lambda^2 c\tau_{\text{photon}}} \frac{1}{g(\omega)}
\]  \hspace{1cm} (25)

If the gain condition is met the number of photons increases exponentially with each pass. The rate of stimulated emission increases with the number of photons passing through the medium. After a certain number of trips the rate of stimulated emission will cancel out the population inversion and gain will saturate. At such a steady state oscillation state a phase shift condition supresses any transverse axial laser modes which do not have a round trip phase shift equal to an integer multiple of \(2\pi c/2L\). \(L\) is the cavity length and \(c\) is the speed of light. Cavities are generally designed to favour a TEM\(_{00}\), or Gaussian, mode. If one of the end mirrors is partially transmitting a coherent, collimated beam will be emitted.
For material processing applications a temporally short, intense burst of light is more useful than the same energy spread over a longer laser pulse. If cavity losses are initially held at an artificially high value while the pumping process is in effect a substantial population inversion can be achieved. If the cavity losses are suddenly decreased the oscillations in the cavity are rapidly amplified to an intense pulse and the cavity is saturated. This technique is known as Q-switching. Pulse durations of tens of nanoseconds can be achieved, depending on the cavity lifetime. A Q-switched laser can achieve peak powers four orders of magnitude higher than the same cavity and laser medium operating in a CW mode. Lasers used in this study are Q-switched using electooptic techniques. A Pockel’s cell and a polarising prism are arranged in the cavity. The Pockel’s cell can rapidly alter the loss in the cavity by manipulating the polarisation dependent reflection or transmission at the prism.

To achieve pulses of picosecond or femtosecond temporal duration the oscillator cavity must be mode-locked. Due to the wave nature of light constructive and destructive interference will take place in the cavity leading to the formation of a standing wave. The standing wave represents the allowed longitudinal modes of the cavity. Other modes in the cavity are suppressed by destructive interference. The number of allowed modes in a cavity of length $L$ is $q=\frac{2L}{\lambda}$. The period of the allowed modes is $T=\frac{2L}{c}$. If the cavity is designed such that each mode operates at a fixed phase the modes will constructively interfere with one another, summing into an intense pulse. This technique is known as mode-locking. The duration of the pulse is determined by the number of modes which can be supported in the outputted bandwidth of the laser medium. Large bandwidth materials can achieve smaller pulse durations. To achieve ultrashort pulse durations the laser bandwidth is typically tens of nanometres. This significant bandwidth leads to chromatic dispersion effects in the oscillator which must be compensated for. The ultrashort laser used in this study is mode-locked using the Kerr-lens mode-locking technique. Due to the non-linear dependence of the refractive index high intensity short pulses in the oscillator will behave differently to CW pulses. A non-linear SESAM mirror is used in the cavity to suppress CW operation and achieve modelocking.

### 2.2.3 Laser Amplifier

A laser amplifier takes an input optical signal and outputs an identical signal but with higher power. High power lasers require separate amplifiers as pumping a laser oscillator to reach such high powers causes stability issues. Temperature control and optical damage are the
limiting factors. To achieve high power, high quality, laser outputs a stable signal is taken from a laser oscillator and passed through a laser amplifier. A laser amplifier is similar to a laser oscillator but with alternative feedback mechanisms. A laser medium is pumped to achieve population inversion and stimulated emission will take place if photons of the correct energy propagate through. The laser medium can be a crystal or a doped optical fibre.

Single or multiple passes through the amplifier may be required depending on the laser characteristics. For ultrashort lasers, which are based on broadband gain media, the gain per pass is low. In this case regenerative amplifiers are used. An electrooptic switch traps a pulse inside an optical resonator, which contains the gain medium. Multiple passes are made until the pulse saturates the medium. The pulse is then switched out of the amplifier, using the same electrooptic switch, and directed towards its next target.

### 2.2.4 Pulse Stretcher and Compressor

Amplifying an ultrashort pulse to a level useful for material processing is more challenging than the short pulse case. During amplification the pulse will reach sufficiently high intensities for non-linear effects to occur (see section 2.1.4). The pulse will self-focus in the laser medium causing beam distortion and, potentially, optical damage of the medium. This issue limited the peak power of ultrashort lasers until a solution was developed in the 1980s. Strickland et al [19] found ultrashort pulses could be temporally stretched and compressed using a pair of dispersion gratings, with negligible distortion.

Prior to amplification the pulse is stretched using a pair of dispersion gratings. The dispersion is wavelength dependent and so longer wavelengths will have an increased path length relative to shorter wavelength. Consequently longer wavelengths will be delayed causing a temporal stretching of the pulse. The pulse is now spectrally chirped. For ultrashort lasers the pulse is typically stretched to several hundred picoseconds. The intensity of the pulse is reduced below the nonlinear threshold and the pulse can now be amplified, as discussed in section 2.2.3, without beam distortion. After amplification another set of dispersion gratings is used to reverse the temporal stretching and return the pulse to its original duration. Alternatively a pair of prisms can be used to stretch and compress the pulse.
2.2.5 Harmonic Generation

Solid state lasers typically output at near IR wavelengths. For some applications it is preferable to use light with a shorter wavelength. Harmonic generation is a nonlinear polarisation effect which allows the optical frequency of a laser beam to be doubled, tripled or quadrupled (see section 2.1.4). Using this method a laser beam with a wavelength of 1030nm can be frequency quadrupled to 266nm.

Frequency doubling is a second-order nonlinearity effect which occurs when a strong electric field causes a nonlinear polarisation wave in a harmonic crystal. This wave oscillates at twice the optical frequency as the laser pulse which provoked it. The polarisation wave emits an electromagnetic wave at the doubled frequency. Two IR photons are required to produce a single green photon. The efficiency of the conversion process is strongly dependent on the phase matching of pulses generated in different positions in the crystal. Consequently the crystal dimensions and orientation must be carefully controlled to maximise conversion efficiency. Typically the conversion efficiency is ~50%. With idealised conditions 85% conversion efficiency has been demonstrated[20].

Higher order harmonics are generated in a cascade process. For frequency tripling the input beam is first frequency doubled to produce a green beam. A combination of the original IR beam and the green beam then combine to produce a nonlinear polarisation wave in a harmonic crystal. In this case the frequency of the polarisation wave, and the emitted electromagnetic radiation, is equal to the sum of the frequencies of the two input beams. One IR and one green photon is required to produce a UV photon. This is known as sum frequency generation. The third-order nonlinearity is too small for practical production of UV light directly from an IR input beam.

Even order nonlinear effects, such as optical frequency conversion, occur only in transparent crystals which lack inversion symmetry. Typical crystal materials used are borates, such as lithium triborate, niobium based crystals, such as potassium niobate. Crystals degrade over time due to optical damage. It is possible to reorientate the crystal to irradiate a fresh site. Harmonic crystals are typically hydroscopic and will degrade over time due to moisture in the air.
2.3 Laser Material Interactions

Laser scribing of glass requires significant coupling of optical energy into the substrate. This section discusses the coupling of laser energy into a material, in particular a transparent material. The subsequent response of the material to the laser pulse and material removal mechanisms are reviewed.

2.3.1 Defect Absorption

Glass processing with short pulse lasers is limited due to the negligible linear absorption of UV, VIS and near IR wavelengths ($\alpha<<1\text{cm}^{-1}$) in glass due to the large bandgap, typically $\sim 4\text{eV}$ [21]. For linear absorption to occur a laser with a wavelength of approximately 310nm would be required. In this case absorption takes place through bulk defects, surface states and quasi-free seed electrons. In the long pulse regime the seed electrons, which are required for the avalanche ionization to take place, are only available through thermally excited electrons or defect states in the material. These defect states and thermally excited electrons are not uniformly distributed over the surface. Consequently the material damage threshold in the nanosecond regime is stochastic in nature. No precisely defined laser-induced damage threshold exists for laser pulses longer than approximately 10ps [22].

2.3.2 Non-Linear Absorption

Non-linear absorption mechanisms can couple laser energy into a material which is normally transparent to the particular wavelength [23]. The initial interaction is mediated by photoionisation. Depending on the laser parameters there are two types of photoionisation which can take place. At low frequencies and high intensities nonlinear photoionisation occurs predominantly by tunnelling ionisation. Here the strong electric field associated with the incident laser interacts with the Coulombic binding force holding the electron to its host atom. This interaction suppresses the Coulombic potential well and, if the applied electric field is sufficiently strong, there is a probability that bound electrons can tunnel through the shortened barrier and become free. For a high laser frequency we are in the multiphoton ionisation regime. Two or more photons are absorbed simultaneously and the sum of their energies is sufficient to promote an electron from the valence band to the conduction band (Figure 2.3).
The theoretical transition between multiphoton ionization and tunnelling ionization is described by Keldysh [24]. Expressions are given for the probability of ionisation of atoms in the electric field of a strong electromagnetic wave. For the low frequency case the expressions describe the probability of tunnelling ionisation. At high frequencies they describe multiphoton absorption processes. The transition between the two is described by the Keldysh parameter ($\gamma_k$) (26). $\omega$ is the laser frequency, $I$ is the laser intensity, $m_e$ and $e$ are electron mass and charge, $c$ is the speed of light, $n$ is the refractive index of the material, $E_g$ is the band gap of the material and $\varepsilon_0$ is the permittivity of free space.

$$\gamma_k = \frac{\omega}{e} \left[ \frac{m_e c n \varepsilon_0 E_g}{I} \right]^{1/2}$$ (26)

A value of $\gamma_k << 1$ is indicative of the tunnelling regime. In the case where $\gamma_k >> 1$, we are in the multiphoton absorption regime. There is an intermediate regime for $\gamma_k \approx 1$ where photoionisation takes place as a mixture of tunnelling and multiphoton ionisation. Lenzner et al [25] studied femtosecond optical breakdown in dielectrics and found that, for pulse durations <100fs, the observed multiphoton ionisation rates were orders of magnitude lower than predicted by Keldysh. Lenzner postulates that free electron collisions and other unidentified mechanisms strongly interfere with multiphoton ionisation in dielectrics near breakdown. This low multiphoton ionisation rate results in anomalously high breakdown thresholds. Contrary to this Stuart et al [26] demonstrate results in agreement with the Keldysh model.
Figure 2.3: Schematic of nonlinear photoionisation processes. (a) shows multiphoton ionisation, two or more photons are absorbed simultaneously to excite an electron to the conduction band. (b) shows avalanche ionisation, an initially free electron absorbs photons through free carrier absorption. The electron then excites an additional electron to the conduction band through impact ionisation while remaining in the conduction band itself.

Free electrons generated through photoionisation are highly absorbing of further photons through inverse bremsstrahlung. Excited free electrons can ionise additional electrons in a positive feedback process known as avalanche ionisation. Free electrons cannot completely couple energy into the lattice during the laser pulse and will accumulate in the laser interaction zone. A rate equation with decay terms is used to describe the free electron density \( N_e \) evolution (27). The first term on the right hand side accounts for electrons excited by multiphoton ionisation. \( \sigma_n \) is the n-photon absorption cross section. \( n \) is the smallest number of photons which together have energy greater than the material bandgap. The second term is the avalanche ionisation term, \( \varsigma_a \) is the avalanche coefficient. The last term accounts for free electron decay where \( k^{rec} \) is the electron-hole recombination rate.

\[
\frac{dN_e}{dt} = \sigma_n I + \varsigma_a I N_e - k^{rec} N_e \tag{27}
\]

The damage threshold \( \varphi_{th} \) of a material is defined as the applied laser fluence which produces observable, irreversible changes in the material. The damage threshold is exponentially dependent on the pulse duration \( \tau_l \) of the incident laser \( \varphi_{th} \propto \tau_l^x \), where \( x \) is some exponent. For long to short pulse lasers an \( x=0.5 \) has been reported [27], consistent with a thermal process regulated by heat transport in the material. At pulse durations <10ps this
dependence breaks down [26]. The damage threshold is no longer determined by heat conduction. Multiphoton absorption and impact ionisation leading to optical breakdown is now the dominant mechanism. The dynamic relationship between the ionisation processes has been modelled by several authors [25, 26, 28-31]. Various functions are used to represent the electron distribution (Fokker–Planck, Fermi). The criteria for material damage to occur is also considered. Some authors take this to be a free electron density threshold, while others take it as a certain lattice temperature. The models are generally accurate over a certain range but the difficulty remains to form a valid model over a large energy and free electron density range.

The optical properties of an ionised dielectric surface will change dynamically over the course of the laser pulse with the effects peaking approximately 100–500fs after the commencement of the laser material interaction[28, 32]. The surface plasma will strongly attenuate the incident beam through linear absorption and a fluence dependent increase in surface reflectivity [32]. The optical properties of a free electron plasma are accurately described by the Drude-Lorentz model. We begin by considering the harmonic oscillator expression discussed previously (3). As we are now dealing with free electrons we can neglect the restoring force term. The electron displacement \(x\) can be expressed as (28).

\[ x = \frac{eE}{m_0(\omega^2 + i\gamma\omega)} \]  

(28)

Given that the electric displacement is related to the polarisation by \(D = \varepsilon_0E + P\) and for isotropic materials \(D = \varepsilon_0\varepsilon_rE\) we can derive an expression for the relative permittivity (29).

\[ \varepsilon_r(\omega) = 1 - \frac{Ne^2}{\varepsilon_0m_0} \frac{1}{(\omega^2 + i\gamma\omega)} = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)} \]  

(29)

\(\omega_p\) is the plasma frequency and is defined as \(\omega_p = \sqrt{Ne^2/\varepsilon_0m_0}\). Equation (29) can be used to determine the refractive index \((n = \sqrt{\varepsilon_r})\) and therefore the reflectivity of the free electron plasma. The reflectivity for a lightly damped system \((\gamma = 0)\) is plotted in Figure 2.4.
Figure 2.4: Plot of the reflectivity of a free electron plasma illuminated with 1030nm light, according to the Drude-Lorentz model. The free electron density which gives a plasma frequency corresponding to IR 1030nm light is indicated.

The damping term ($\gamma$) is related to the electron momentum ($m_0dx/dt$). We can replace the damping rate with a momentum scattering time term ($\gamma=1/\tau$). The electric field of a laser oscillates as a plane wave leading to electronic displacements and electronic velocities in the form of a plane wave. Solving the equation of motion (3) for solutions of this form we obtain (30).

$$v(t) = \frac{-e\tau}{m_0} \frac{1}{1 - i\omega\tau} E(t)$$ (30)

The current density of the oscillating electric field is considered next. The current density is related to the velocity and electric field by $j=-Ne\nu=\sigma E$ where $\sigma$ is the electrical conductivity. Combining this with equation (29) we obtain an expression for the frequency dependence of the AC conductivity (31). $\sigma_0$ is the DC conductivity and is given by $\sigma_0=Ne^2\tau/m_0$.

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}$$ (31)

Combining (29) and (31) we obtain an expression for the dielectric constant in terms of the conductivity, (32).

$$\varepsilon_r(\omega) = 1 + \frac{i\sigma(\omega)}{\varepsilon_0\omega}$$ (32)
Breakdown of the material occurs when the density of free electrons reaches a critical value. This is typically taken as the density where the plasma becomes reflecting of IR wavelengths, approximately $10^{21}$ cm$^{-3}$\[26\] (see Figure 2.4). Excited electrons will equilibrate with the lattice within a few picoseconds\[23\]. Rapid heating of the substrate leads to melting, vaporisation and material ejection.

Deterministic damage thresholds in the ultrashort regime can be defined for glass due to the self-seeded avalanche ionization, facilitated by free electrons produced by nonlinear photoionisation. Incubation effects have been observed in several types of glass \[31, 33\]. Irradiation of a dielectric surface with fluences just below the ablation threshold will initially have no effect but repeated irradiation will lead to formation of colour centres, followed eventually by ablation. Colour centres will cause higher absorption of the laser energy.

The propagation of a high intensity laser pulse through a transparent material is perturbed temporally, spatially and spectrally (see section 2.1.4) by the intensity dependence of the refractive index $n(I)=n_0+n_2I$. The nonlinear refractive index can be positive or negative. Ultrashort lasers have extremely high peak intensities so the non-linear refractive index is important in understanding how the light propagates in glass. Glezer et al \[34\] estimated the change in refractive index to be in the range 0.05 - 0.45 by examining an array of voxels written 100μm below the surface of fused silica by a tightly focused 100fs laser. The intensity is not evenly distributed spatially or temporally. This leads to self-focusing and self-phase modulation.

The nonlinear refractive index ($n_2$) is positive in most materials. Considering a Gaussian shaped laser spot, we have a higher refractive index in the centre (where intensity is highest) and a lower refractive index towards the edges. This spatially dependent refractive index is equivalent to a positive lens. This leads to focusing of the laser as it propagates through the medium. The strength of the lens is related to the laser power, as laser power is increased the self-focusing effect becomes larger until, at a critical power ($P_{cr}$), it reaches an equilibrium state with diffraction and a filament is formed \[35\].

$$P_{cr} = \frac{3.77\lambda^2}{8\pi n_0 n_2} \quad (33)$$

$\lambda$ is the wavelength of the laser, and $n_0$ is the linear part of the refractive index. $P_{cr}$ is usually on the order of MW. For laser powers greater than $P_{cr}$, steady-state theoretical analysis predicts that the pulse will undergo catastrophic collapse \[36\] due to self-focusing. In reality...
this does not occur. As the laser self-focuses its intensity will increase until it is sufficiently high to non-linearly ionize the material. The plasma formed will contribute negatively to the refractive index cancelling the positive contribution from the intensity-dependent refractive index and preventing collapse of the pulse [36].

Saliminia et al [37] studied filamentation in fused silica with femtosecond pulses. A number of observations were made. Even at very tight focusing filamentation was observed giving rise to repeated elongated zones beyond the geometrical focus. Filament length was observed to increase with pulse energy with its leading edge moving towards the objective lens. At higher laser energies multiple filaments were observed, which fuse towards the geometrical focus. Saliminia postulated that these could arise from inhomogeneities in the laser beams spatial profile triggering localized small scale self-focusing. Some authors have demonstrated filamentation based thin glass scribing processes [38, 39].

Self-focusing is the enabling mechanism for Kerr lens mode locking. This method of mode locking enables generation of pulses of light with durations as low as a femtosecond[40]. Due to the non-uniform intensity distribution of the laser pulse it experiences non-linear refractive index effects in the gain medium. The cavity can be designed to favour the pulsed laser modes over the CW modes resulting in a mode locked laser[40].

A laser pulse has an uneven intensity distribution over time. Consequently the non-linear refractive index causes a perturbation of the temporal shape of the pulse. This generally leads to a spectral broadening of the pulse and is one of the mechanisms leading to white-light continuum generation. The spectrum of a low power loosely focused femtosecond pulse incident on a transparent material can be observed broadening to cover the entire visible range [41].

2.3.3 Material Removal Mechanisms

Thermalisation of the absorbed energy into the material is characterised by a thermal diffusion length, this is related to the square root of the pulse duration ($\tau$) and the thermal diffusivity ($D_l$): $l_T \approx 2 \sqrt{D_l \tau}$. For long pulses conduction of heat through the lattice is the controlling factor. Material removal takes place mainly through melting and vaporisation of the substrate, if the laser intensity is sufficient. A dense vapour plume will be formed. Depending on the laser intensity the plume can become ionized by the laser and be transformed into a plasma. The
plasma will attenuate the incident laser. As species leave the surface they carry away some kinetic energy and internal energy[42].

For pulse durations >20ps a $\sqrt{t}$ dependence for the damage threshold has been reported[27], indicating a thermally controlled process. As pulse durations are decreased below this threshold a departure from this dependence has been found [26, 43, 44]. Stuart et al [26] found changes in the morphology between short pulse craters and ultrashort pulse craters indicated the transition from a thermally dominated regime (short pulse) to an ablative regime dominated by non-linear absorption (ultrashort pulse). A model based around multiphoton ionisation providing seed electrons for the avalanche ionisation process predicts the ultrashort pulse damage thresholds in good agreement with experimental results. The photoexcitation pathway responsible for ablation is dependent on material properties and laser parameters. The absorbed energy is dissipated through the material causing material removal which will take place mostly after the pulse duration. There exist two major material removal mechanisms: thermal vaporisation, accompanied by surface fragmentation, and Coulomb explosion. In most cases the two competing mechanisms coexist in material removal. The dominant mechanism depends on material properties, laser intensity, wavelength and number of pulses [45]. Laser ablation begins after a delay of typically 1 to several tens of picoseconds. This indicates that plasma shielding has little influence on the ablation process as the ablation initiates before plasma plume expansion has occurred.
Figure 2.5: Diagram illustrating the difference between short and ultrashort pulse laser ablation. The free electrons required to initiate ablation in the interaction volume are randomly distributed in the short pulse case. For ultrashort lasers they are generated by the laser itself and ablation is highly reproducible. The ultrashort pulse durations prohibits thermal diffusion occurring during the laser pulse eliminating edge burrs and minimising the heat affected zone.

Thermal vaporisation can take place through normal boiling or phase explosion. For moderate laser intensities and fluences just above the damage threshold of the material normal boiling will occur. The mismatch between lattice heating time and lattice expansion time leads to isochoric heating of the interaction zone. This leads to thermoelastic pressures in the material which can reach several GPa and cause fragmentation around the laser interaction zone. Fragmentation is undesirable as it reduces the resolution of the laser process. Relaxation of this stress gives rise to rapid surface expansion. This leads to a stress wave propagating into the material, surface deformations and void formation below the surface [42]. This pressure causes tensile stress in the material which favours void formation in the melted material. This theory is supported by ultrafast microinterferometry measurements in gold [46] and GaAs [47] ablated at fluences just above the material damage threshold. Molecular dynamic simulations also reach similar conclusions [48]. The approach here is to model the material on an atomic scale, with each spherical atom being free to move in three dimensions. The incident laser deposits energy into the system which imparts a velocity to each atom in a random direction. Typically systems with $10^8$ atoms are simulated, limited by computational constraints.
As the laser intensity is increased phase explosion becomes dominant mechanism. The melt becomes overheated by the laser into an unstable thermodynamic state and undergoes a rapid transition to a mixed gaseous/liquid state [42]. Bulgakova et al [49] found materials exhibit a second threshold where thermal vaporisation moves from normal boiling to phase explosion. The second threshold is accompanied by an increase in the ablation rate. The rapid heating of the material takes place under almost isochoric conditions, leading to significant stress in the interaction volume. Relaxation of this stress leads to thermomechanical ablation of the substrate [42]. Thermomechanical ablation is unpredictable and to be avoided in micromachining applications.

Coulomb explosion becomes dominant in non-metals for high-intensity laser irradiation. The emitted plume becomes ionised leading to strong energy coupling to the plasma layer. This yields intense photoemission of electrons which results in a local accumulation of positive charges and a corresponding electric field. The electric field can overcome the binding forces within the lattice and pull ions out of the material [42]. Charge accumulation, and thus Coulomb explosion, is suppressed in metals due to fast electron transport properties. Coulomb explosion results in a much smaller ablation depths compared with thermal vaporisation and leaves a smoother ablated surface [50]. Stoian et al [51] measured the time of flight of emitted charged species from a silica substrate irradiated by a 800nm wavelength, 100fs laser at a fluence slightly above the damage threshold. The high velocity of emitted ions (20km/s) indicates that Coulomb explosion governs material removal in this regime.

2.4 Prior Art in Thin Glass Processing
Lasers are versatile material processing tools and offer numerous methods for glass cutting. In this section we review the current state of the art for laser processing of glass for a variety of laser sources. Non-laser based methods for glass processing are also discussed.

2.4.1 CW and Short Pulse Laser Processing
Initially laser techniques for glass processing involved a scribe and break process, similar to mechanical processing[52]. The substrate is scribed with a focused beam and force is applied to the scribe to fracture the substrate. Similar to mechanical cutting there will be chipping along the cut edge which may require post process polishing. Du et al [53] investigated this process
using an IR laser with a 6ns pulse duration, scribing 4mm glass samples at a speed of 3m/s. Surface roughness is 10μm, the type of roughness measurement is unspecified.

Controlled fracture of glass can be achieved using a CO₂ laser to locally heat the glass[54]. CO₂ lasers typically output at 10.6μm which couples strongly to vibrational modes in silica molecules. Optical energy will be absorbed in the glass surface leading to rapid heating. Controlled fracture techniques are based on the fact that the tensile fracture stress of glass is lower than the compressive fracture stress due to flaws in glass being unable to amplify compressive stresses[3](see section 2.5.1). A glass substrate containing an edge crack is locally heated by a CO₂ laser to a temperature below the glass transition temperature, causing compressive stresses in the substrate, insufficient to cause fracture. The heated region will cool rapidly, driven by large temperature gradients. Rapid cooling leads to tensile stress in the material which cause extension of the pre-existing edge crack along the line heated by the laser. Due to symmetric gradients being produced on either side of the heated region crack propagation can be unpredictable. There is also some time delay between the laser heating and crack extension.

The uniformity of this technique was improved by Kondratenko[55]. Subsequent to laser heating a coolant air jet is applied to heated region. Rapid cooling causes the stress to become tensile and cause the pre-existing crack to extend. The tensile stress peaks in the centre of the laser spot ensuring the crack extension is controllable. The overall tensile stress is higher than without the coolant increasing the processing speed. Optimum process parameters depending on substrate thickness have been examined by Yamamoto et al [56]. Mechanical force is usually required to ensure the crack has propagated through the entire substrate. This method is widely used in industry for processing glass of half a millimetre to several millimetres thickness. Processing speeds of 300mm/s are reported for 1mm thick soda lime glass[57]. It is possible to cut curves using this method, however, the shape must begin and end at an edge. While the equipment is more costly than a mechanical cutter the processing speed and cut quality are higher. Other authors have experimented at optimising this process[58, 59]. Kang et al [58] found that a liquid coolant resulted in a faster cutting process but nonuniform edge quality due to the discontinuity of the liquid stream. Tsai et al [59] showed an improvement in cutting speed and quality by pre bending the substrate.

Previous works have investigated controlled fracture techniques combining mechanical/laser scribing with laser induced thermal stress to bring about controlled fracture
of the glass [60-63]. Verheyen et al [60] showed it was possible to cut glass substrates with thicknesses greater than 10mm. This method involved first scoring the surface with a scoring wheel under a small applied load. The scored line was then heated with a CO₂ laser causing fracture along the predefined line. Tsai [63] achieved similar results using a diamond scribe and CO₂ laser. Jiao [61] and Tsai [62] investigated dual laser setups where a Nd:YAG laser was used to scribe glass followed by a defocused CO₂ laser to induce fracture.

A heating and vaporisation technique for glass was investigated by Ozkan et al [64]. A groove was produced in 1mm thick BK7 glass by heating the material past the vaporisation point using a microsecond CO₂ laser and a Q-switched nanosecond CO₂ laser. Cracking around the groove was apparent even for the short pulse laser. This method is unsuitable for processing thin glass as the thermal shock causes fracture of the material. Chui et al [65] investigate a vaporisation process, using a CO₂ laser, while the glass is held at 500°C in a furnace. As the entire substrate is pre heated the thermal shock produced by the laser heating, and hence cracking, will be reduced.

A full body laser cut is achieved by repeatedly scanning a focused laser beam over the glass surface[57]. The laser fluence must be sufficient to ablate the material. Surface ablation of fused silica using a 266nm laser with a 30ns pulse duration has been reported by Ozkan [64]. The photon energy is sufficient for partial linear absorption of the laser in the material. Chipping and cracking along the cut edge is observed and attributed to forceful material ejection caused by a surface plasma. Similar tests were carried out on BK7 glass, which has increased UV absorption due to dopants. A marked increase in processing quality due to the increased absorption was found. The impact on material removal rates is not discussed. Nikumb et al [13] found optimal process parameters for glass processing using a 512nm wavelength 30ns laser. By using a slightly defocused laser with a low repetition rate and scan speed, thermal loading and thus chipping in the substrate can be reduced. However the processing speed is too low for industrial applications. Karnakis et al [66] investigated borosilicate glass processing using a nanosecond 255nm wavelength excimer laser. Clean and well defined 30μm wide channels were produced. Some micron scale burr was formed on the edge of the channel. Material removal rates are too low for an effective glass cutting process. After 10 laser passes, at a scan speed of 10mm/s, a depth of 50μm has been reached. The low repetition rate of excimer lasers limits their use in glass cutting processes.
Coupling of laser energy into glass can be improved using a dual wavelength hybrid technique. Obata et al [67] showed an improvement in feature quality and processing speed when using a dual excimer laser, multi-wavelength process. 10ns pulses from a 248nm KrF laser and a 157nm F₂ laser were simultaneously applied to a fused silica substrate. Results showed ablation occurring at fluences below the damage threshold of the material with orders of magnitude greater material removal rates. This was attributed to the high energy F₂ laser pulse exciting electrons to defect states where they readily absorb the KrF laser pulse.

2.4.2 Ultrashort Pulse Laser Processing

Ultrashort pulse lasers are suitable for thin glass processing due to non-linear absorption mechanisms and minimal thermal effects. Ablative surface cutting techniques are possible by scanning a focused laser along the glass surface. Edge quality of cuts is reasonable although processing speeds are poor[12, 13, 64, 66, 68-70]. Nolte et al [12] examined full body cuts made in 75μm thick glass using an ultrashort laser operating at 800nm. The cut face typically has a contoured surface, indicating that localised melting took place[70]. Single pass cuts were made by scanning the focused laser at a speed of 0.5mm/s with a pulse energy of 500μJ. The cut edge is reasonable with some chipping occurring on the rear surface. Microspheres are formed on the cut face due to material redeposition and localised melting followed by resolidification. Lowering the pulse energy to 100μJ was found to improve cut face roughness at the expense of processing speed. This is in agreement with a similar study by Ameer-Beg et al [68] who also showed that the laser wavelength has little effect on processing speed and quality. Ozkan [64] investigated the effect of pulse repetition rate on the cut quality. Processing at 25kHz produced less edge chipping than 250kHz due to decreased thermal loading.

Lasers which emit linearly polarised light may undergo anisotropic interactions with materials. When the laser is incident on a substrate at an angle the plane of incidence is defined by a vector normal to the trench walls and a vector parallel to the propagation direction of the laser (see Figure 4.17). If the laser polarisation is parallel to this plane it is referred to as P polarised; if the laser polarisation is perpendicular to this plane it is S polarised. Vanagas et al [69] carried out glass scribing experiments using a circularly polarised femtosecond laser. Spall-like damage regions were observed at the rear surface of the glass after scribing. This damage was attributed to Rayleigh waves produced by the plasma ablation pressure. Extensive studies have been completed on hole geometries and morphologies created during polarised
ultrashort pulse ablation. Nolte et al [71] manufactured high aspect ratio holes in stainless steel using linearly polarised 170 fs laser pulses. Bulges were observed around the exit hole orientated perpendicular to the polarisation of the laser. Nolte concluded that the bulges are due to polarisation dependent reflections inside the hole and implemented a ‘polarisation trepanning’ technique to improve the uniformity of the exit hole. Kamalu [72] found the laser cutting speed of steel varied by a factor of two depending on the orientation of the linear polarisation. The cutting speed was highest when the polarisation was orientated parallel to the plane of incidence (P polarised) at the cut wall. P polarised light has a lower reflectivity than S polarised light, especially for glancing angles and for this reason it will be preferentially absorbed in the substrate leading to increased cutting speeds.

Other non-polarisation related ablation effects have been observed. Klimentov et al [73] found severe deviation of the crater geometry when percussion drilling steel with 130 fs pulses. The effect was explained by dynamic non-linear propagation of the laser pulse in the ambient atmosphere before the geometrical focus, which distorted the beam profile from Gaussian to a wide angle cone. There is also some evidence of the ablated material lingering in the interaction zone causing further distortion to beam profiles of subsequent pulses.

The well-defined damage threshold associated with non-linear absorption mechanisms mean an ultrashort laser can be focused inside a bulk glass substrate with absorption occurring only at the focal point. With proper selection of laser parameters a positive change in refractive index can be created in the glass. Glezer et al [74] initially applied the technique, using low energy femtosecond pulses, to produce local surface and bulk changes of refractive index in transparent materials for optical storage devices. Schaffer et al [75] show that this is possible even with unamplified ultrashort pulses with 5nJ of energy per pulse. The same authors also report on a thermal mechanism for producing bulk changes in refractive index using a high repetition rate ultrashort laser [76]. By translating the sample relative to the laser beam a waveguide can be written into the glass [77, 78].

Bulk breakdown of glass due to single pulse laser induced microexplosion has been widely reported [79-84]. The laser is focused into the bulk of the glass and can be translated to produce conjoined voids. Ablation cannot occur as the excitation is contained inside the bulk of the material. The non-linear absorption mechanisms create very high temperature and pressure gradients inside the focal region forcing material into the surroundings. This creates a void surrounded by a local high density region. Using tight focusing optics Gamaly et al [83]
produced bulk voids in glass substrates and found the size of the void scaled with pulse energy. Schaffer et al [82] demonstrate conical voids formed with low NA focusing optics. The use of high repetition rate lasers increases processing speed however localised heating and melting may occur if the pulse period is shorter than the characteristic thermal diffusion time [75, 76]. For a high NA focusing objective the time for thermal diffusion out of the focal volume to occur is about 1μs[85]. A process has been patented [86] which uses picosecond duration pulses to produce bulk voids in a glass substrate. The laser operates at MHz repetition rates and is scanned so that pulse overlap is <20%. This scribe defines a weakened plane which can be fractured with mechanical force to complete the cut. An alternative technique for producing bulk voids involves photosensitising the glass with ultrashort laser irradiation followed by HF etching [84]. The voids must be connected to the surface at a point to allow the acidic solution to enter. A similar technique involves processing the glass in a water bath to assist in the removal of debris from a laser produced micro channel [79, 80]. By combining waveguides with channels for microfluidic applications highly functional ‘lab-on-a-chip’ devices [87] can be fabricated for biosensing applications.

Bessel beams maintain a long longitudinal focus due to positive self-interference. The invariant transverse intensity profile can reach several millimetres in length. This eliminates the need for repositioning of the focal point when machining a material. Tsai et al [88] investigated the use of Bessel beams for multi-shot laser glass scribing using a 120fs laser. An axicon lens was used to transform the beam from a Gaussian to a Bessel intensity distribution. The diameter of the beam was 2.03μm and the length was 2.12mm. 100μm thick glass was scribed at a processing speed of 1mm/s. The speed was limited by the 1kHz repetition rate used. The scribe had a width of approximately 2μm. After mechanical fracture the cut face roughness was Ra=27.6nm with submicron chipping. Bhuyan et al [89] improved the processing speed by using a higher power, higher repetition rate laser in a single-shot process. Scribing speeds of 270mm/s are reported for 700μm thick aluminosilicate glass.

Combining pulses of differing wavelengths has been shown to be beneficial to ultrashort laser material processing. Yu et al [90] investigated the effect of irradiating fused silica with 266nm, and 800nm femtosecond laser pulses with a variable delay between pulses. A 71% decrease in the UV damage threshold was observed. This peak value was found when the NIR pulse was delayed by 60fs after the UV pulse. The UV pulse generates free electrons through two photon absorption. The free electrons readily absorb the subsequent NIR pulse.
An increase in material removal rates was also found. This effect has also been observed in silicon [91].

The state of the art for laser processing of thin glass has seen a paradigm shift from standard ablative cutting techniques towards novel filamentation based methods. Due to the considerable value chain associated with high speed and high quality processing of thin glass significant resources have been devoted to the issue. Several authors report on filamentation based methods for forming elongated voids in glass substrates [92-96]. Filamentation occurs due to dynamic reciprocation between nonlinear Kerr self-focusing and plasma defocusing in the focal region [97]. The laser can be translated across the sample to form an array of voids which define a weakened plane. A prominent filamentation method for thin glass processing has been demonstrated by Hossieni et al [38]. A glass substrate with thickness >100μm is irradiated with tightly focused ultrashort pulses in a burst train mode. The interval between pulses in a burst of pulses is of the order of 20ns. This interval is short enough that the material remains in an excited state between pulses increasing filament length. By translating the laser across the sample a series of elongated hollows are formed aligned with depth in the glass (see Figure 2.6). The elongated hollows are effective stress raisers allowing the substrate to be fractured at much lower tensile loads. Processing speeds of 300mm/s are reported [98]. Self-cleaving of tempered glass after irradiation has also been demonstrated. The filament length is sufficient to reach the tensile stress region in the middle layer of the glass. This tensile stress along with the stress raising property of the filament causes spontaneous fracture of the substrate. Another proprietary process which uses a 400fs laser to irradiate a glass substrate has been reported [39]. The details of the process are undisclosed, however it is likely a filamentation process which also uses the tensile stress region in tempered glass to achieve self-cleaving. Speeds of 1m/s are demonstrated with bend strength of 650MPa for tempered glass. Filamentation processes are less suitable for thin glass as the laser typically requires at least 50μm of material in which to propagate for filamentation to occur [97, 99].
2.4.3 Other Processing Methods

Glass can be mechanically cut using specialist tools such as a diamond scribe or tungsten carbide cutting wheel. The process involves two steps: scribing and snapping [100]. The glass is scribed resulting in a stress induced crack. The scribe is characterised by three distinct regions: the cutting score, the median crack and lateral cracks. The cutting score is the region where the wheel contacts the glass causing plastic deformation of the surface. The median crack is aligned with the cutting score and directed orthogonally to the glass surface. Lateral cracks extend from the cutting score along the glass surface. Force is applied to the glass to propagate the median crack through the entire substrate, completing the cut.

Several parametric studies of the mechanical cutting process have been carried out for thick (>1mm) glass substrates[101-103]. Ono et al [102] found that the median crack depth increased with increasing loads on the scribing wheel. A four point bend test was used to determine the force required to separate the scribed substrate. It was found that a larger median crack requires a lower force to separate the scribed sample. A theoretical model was fitted to the experimental results and indicated that 40% of the stress induced by the scribing process is used during the median crack formation. The remaining stress remains as residual stress along the cutting score and aids in the cleaving of the substrate. When lateral cracking occurs the
Theoretical Background and Literature Review

residual stress is released. Pan et al [101] found a similar relationship between the scribe load and median crack depth. The study found a reduction in surface roughness with increased median crack depth. The amount of lateral cracking also increases with scribe load. Lateral cracking is detrimental to the strength of the cut piece and can cause deviation of the cut line. The scribe load is selected to find an appropriate balance between the median crack length and lateral cracking. Both studies showed with appropriate parameters reasonable quality cuts can be made in 0.7-1.1mm thick glass with scribe speeds of 300mm/s. Kondrashov et al [103] tested the strength of glass samples cut with mechanical wheels. It was found that edge strength increased with scribe load, and thus median crack length, to a certain threshold. Above this edge strength decreased with increasing scribe load due to cracking and chipping around the cutting score. Even with optimum processing parameters the strength of the glass is reduced by an average 60% by the mechanical cutting process [104]. Some of this strength is recoverable through grinding and edge polishing. At the time of writing there are no published experimental studies on the mechanical cutting of ultrathin glass.

Scribing tools are inexpensive, however depending on the requirements the cut glass may require post processing steps to reduce chipping, debris and burrs along the cut edge. Coatings on the surface of the glass may be damaged during the scribing process. A mechanical cutter is unable to cut curved shapes from a glass substrate; scribing is possible only in straight lines. A curve can be approximated by a series of small straight scribes [105], however this process is time consuming and edge chipping will accumulate with each scribe. When mechanically scribing thin glass stray breaking will sometimes occur due to the fragile nature of the glass.

Stress raisers (see section 2.5.1) are utilised by some mechanical glass cutting wheels [106]. These mechanical cutting wheels have a serrated edge which creates perforations along the surface which act as stress raisers assisting in controlled fracture of the substrate (Figure 2.7). Edge quality is improved as the cutting score is periodic rather than continuous.
Thermal induced fracture, as discussed in section 2.4.1, can be achieved by substituting a hot air jet for the CO$_2$ laser source. The mechanism is the same as the laser process, local heating followed by cooling causes tensile stress in the cooling region. Prakash et al [105] carried out a parametric study on glass cutting using this method. A hot air jet, with a temperature of 280°C, was used to heat and fracture glass substrates with thicknesses 2-20mm. Substrates were cooled in atmospheric conditions; the study did not consider the effect of a coolant applied after heating. Cut quality is good with average roughness values of 450nm reported and no cracking or chipping along the edge. The process can be used to cut complex shapes, however the shape must begin and end at the edge of the glass substrate. A millimetre scale edge crack is required to initiate the fracture. Processing speeds are low with speeds of 6.67mm/s reported for 3mm thick glass.

Waterjet cutting is a cutting technique where a mixture of water and an abrasive material is directed through a small nozzle at high pressure onto the glass. Yuan et al [107] studied the cut quality and speed of 1mm thick borosilicate glass processed using this method. An equal parts mixture of 60 and 80 mesh garnet was added to deionised water pressurised at 380Mpa. The solution was forced through a 0.35mm nozzle towards the sample at a speed of
915 m/s. Cutting speeds of 25.4 mm/s are reported with Ra of 10.4 μm. Processing without the abrasive additive in the water results in a reduced cutting speed and increased cut face roughness. Luna at al. [108] analysed stresses in the glass during the waterjet cutting process using a polarscope. No appreciable stress was detected in the study. Any heat generated in the abrasion process is eliminated by the water stream making the process suitable for heat sensitive materials. Consequently the process may be applicable to thin glass, however no studies have been carried out to date. Waterjet processing workstations have capital costs comparable to laser workstations but require a continuous supply of abrasive material and deionised water.

Wet etching is another glass processing technique where acids are used in conjunction with an etch-resistant mask to selectively etch regions of glass. The downside to this process is that hazardous chemicals are required and the process is slow. Nagarah et al [109] report wet etching of fused silica with 49% HF acid. Etched surfaces are extremely smooth with an average roughness value of ~10nm. The etching process takes 7 hours to etch to a depth of 104 μm. The aspect ratio of the etched feature is 0.70.

2.5 Brittle Fracture Theory

Materials typically fracture when stressed beyond a particular threshold. When placed under tensile stress a true brittle material will not deform plastically prior to fracture, contrary to a ductile material. In structural engineering brittle fracture is to be avoided as it will take place rapidly and catastrophically in a structure without any increase in applied stress. Ductile fracture is more forgiving as the plastic deformation which precedes fracture means the crack propagates only as long as the applied stress is increasing. Fracture can be grouped into three modes: I is an opening mode, II is in plane shear mode (sliding), III out of plane shear mode (tearing). This section deals with fracture theory for brittle materials, which include glasses, ceramics and metals cooled below their ductile to brittle transition. In chapter 5 we are concerned mainly with mode I fracture caused by a bending stress in a glass substrate. In chapter 6 other fracture modes are considered. Theory in this section is adapted from Lawn [110] and Anderson [111].
2.5.1 Stress Raisers

A stress raiser is a usually undesirable material defect which concentrates tensile stress in brittle materials at the narrow point of an ellipse or a sharp corner. The stresses around an elliptical flaw in a brittle plate, which is placed under uniform applied tension, were mathematically determined by Inglis [112]. His analysis showed that stresses at the tip of ellipses and sharp corners can be enlarged significantly relative to stress elsewhere in the plate. These features are referred to as stress raisers and are usually undesirable material defects.

Stress concentration can be visualised by considering a two dimensional plate under uniform tensile stress. Stress lines will be distributed uniformly over the entire substrate. If the plate contains an elliptical hollow the stress lines will be directed around it as tensile stress cannot be transmitted through the hollow. Stress lines will overlap at the tip of the ellipse resulting in an amplification of the tensile stress in this region. We consider an elliptical hollow in a plate (Figure 2.8) with major and minor axes of \(2a\) and \(2b\) respectively with a uniform applied tension \(\sigma_A\). To analyse the effect of the hollow on the stress distribution in the plate Inglis assumes that Hooke’s law is valid everywhere in the plate, the hole boundary is free from stress to begin with, the dimensions \(a\) and \(b\) are small relative to the size of the plate and \(a >> b\). Inglis arrives at a remarkably simple expression for the stress concentration factor at the tip of the ellipse where the radius of curvature is at a minimum: \(K=2a/b\).

![Figure 2.8: Substrate under tensile stress \(\sigma_A\) containing an elliptical hollow with major and minor axes of \(2a\) and \(2b\) respectively](image)
For a narrow ellipse the stress concentration factor can become significant. In the limiting case where \( b \) approaches zero then the stress at the crack tip approaches infinity. This is unrealistic as it predicts materials to have near zero strength for very sharp cracks. Nonetheless Inglis’s is valid for cases where \( b > 0 \).

Stress raisers occur naturally in glass. Material scientists were unable to explain the discrepancy between the theoretical fracture stress of glass and the experimental fracture stress. This discrepancy was observed even when great care was taken to produce optically perfect samples. The theoretical fracture strength required to fracture a material is the energy required to break the bonds of the constituent molecules. Silicon and oxygen form a strong covalent bond with an energy of 435kJ, corresponding to a fracture strength of 16GPa [110, 111]. Measured fracture strengths of glass are typically 1000 times lower than this value. Analysis by Griffith concluded that this was due to the submicroscopic flaws in the material which act as stress raisers. Griffith also found a size and aging effect during fracture tests on thin glass fibres. Thinner specimens showed strengths closer to the theoretical limit as the size of the flaws and statistical probability of a flaw occurring decreases with sample dimensions. Freshly drawn fibres were also found to be stronger than fibres which were aged by just 3 hours. The flaws originate from mechanical interactions, such as exposure to hard dust particles in the atmosphere. Other sources of flaws include chemical, thermal and radiant interactions.

### 2.5.2 Thermodynamic Considerations in Fracture

Griffith [113] avoided the sharp crack singularity in Inglis’s analysis by taking a different approach and modelling the crack as a reversible thermodynamic system. The system under consideration is shown in Figure 2.9. The crack is of length \( c_1 \) with crack surface area \( S \) and applied loading \( \sigma_A \).
Figure 2.9: Substrate of unit thickness containing a plane crack with length \( c \) undergoing incremental extension \( dc \) due to applied tensile stress \( \sigma_A \). The domain \( D \) defines the distance travelled by a stress wave propagating from the crack tip in an interval \( t \). The domain \( D \) is circular, only half is shown here for clarity.

The total energy in the system is \( U \) and can be divided into a mechanical energy term \( (U_M) \) and a surface energy term \( (U_S) \). A crack may form (or a pre-existing crack may extend) when total system energy decreases or remains constant. This analysis assumes that the fracture is perfectly brittle and no plastic deformation occurs prior to fracture.

\[
U = U_S + U_M \tag{34}
\]

The surface energy term is the energy required to create a new surface. The higher the free surface energy \( (\gamma_s) \) the more resistive a material is to crack extension. For a substrate of unit thickness the surface energy per crack surface is \( c\gamma_s \). The factor of 2 accounts for an opening crack creating two surfaces (35).

\[
U_S = 2c\gamma_s \tag{35}
\]

The driving force for opening a crack is the mechanical potential energy term \( U_M \). The term for mechanical energy was derived from the Inglis solutions for stress and strain fields, and is given in terms of unit width along the crack front (36).
The surface energy has a linear increase with crack length while the mechanical energy has a quadratic decrease with crack length. To find the equilibrium position we solve for $dU/dc=0$. This is the critical position where fracture will occur, $\sigma_A=\sigma_F$. This is also referred to as the Griffith strength relation (Figure 2.10).

$$\sigma_F = \sqrt{\frac{2E\gamma_s}{\pi c_0}}$$

Figure 2.10: Plot of the critical fracture stress as a function of crack length according to the Griffith strength relation (37).

Figure 2.11 shows a plot of total system energy against crack length. The plot is a hyperbola showing that this equilibrium position is unstable ($d^2U/dc^2<0$). A parabolic plot would indicate a stable equilibrium position.
Figure 2.11: Variation of total system energy with crack length. Plotted parameters are for a silica substrate. Applied tensile stress ($\sigma_A$) for the calculation is $9\text{MPa}$. Equilibrium occurs at $c=1\text{mm}$.

Griffith confirmed his theory, and Inglis’s, experimentally by introducing millimetre scale cracks to thin round tubes and spherical bulbs. The samples were annealed to remove any residual stress and then burst by pumping in water at a controlled pressure. Critical stresses were determined from the water pressure and found to be in reasonable agreement with Griffith energy balance calculation.

### 2.5.3 Kinetic Energy and Crack Bifurcation

The analysis carried out by Griffith considered only static crack systems and did not account for kinetic energy in the system. As an unstable crack expands any surplus energy in the system not used in creating new surfaces will be converted to kinetic energy. The inertia of the separating crack walls adds kinetic energy to the system. Mott [114] added a kinetic energy term to the Griffith energy balance expression to account for this:

$$U = U_M + U_S + U_K$$  \hspace{1cm} (38)

Mott considered a crack in uniform tension (Figure 2.9). The analysis was based on the assumptions that the equations of static elastic theory hold around the moving crack tip, the surface energy remaining independent of crack velocity and the stress wave domain ($D$) extending over the entire sample. Initially the crack is at rest and we have $U_K=0$. This satisfies
the relation that \( dU/dc = 0 \). Using this relation we can eliminate dependence on the surface energy and evaluate \( U_K \).

\[
U_K = \left( \frac{\pi c_l^2 \sigma_A^2}{E} \right) \left( 1 - \frac{c_0}{c_l} \right)^2
\]  \hspace{1cm} (39)

To derive an expression for kinetic energy in terms of crack velocity Mott considered the standard expression for kinetic energy, \( U_k = 0.5mv^2 \). For a moving crack the mass being displaced is the density of the substrate times the crack element displacement in the \( x \) and \( y \) direction integrated over the domain \( D \).

\[
U_K = \frac{1}{2} \rho v^2 \int_D \left( \frac{\delta u_x}{\delta c_l} \right)^2 + \left( \frac{\delta u_y}{\delta c_l} \right)^2 \delta x \delta y
\]  \hspace{1cm} (40)

To solve this integral Mott assumes that the crack element displacements are proportional to \( c \) but also to the strain level in the material. He arrived at an expression for the kinetic energy (41).

\[
U_K = \frac{1}{2} \rho v^2 \left( k c_l^2 \frac{\sigma_A^2}{E^2} \right)
\]  \hspace{1cm} (41)

Where \( k \) is an as of yet undetermined numerical dimensionless constant. By equating these two kinetic energy expressions ((39), (41)) the crack velocity can be written as (42).

\[
v = \sqrt{\frac{E}{\rho}} \sqrt{\frac{2\pi}{k}} \left( 1 - \frac{c_0}{c_l} \right)
\]  \hspace{1cm} (42)

Where \( \sqrt{E/\rho} \) is the Newton Laplace equation for the speed of a Rayleigh wave in a material. Mott’s analysis concludes that the crack tip velocity will asymptotically approach the Rayleigh wave speed in the material as \( c_l \gg c_0 \). Techniques such as high speed photography, ultrasonic and electrical grid methods were developed to measure the propagating crack tip velocities in brittle materials [115-117]. These measured velocities were typically small fractions of the Rayleigh velocity predicted in the analysis by Mott.

The discrepancies between predicted terminal crack velocity and measured terminal crack velocities indicated that further refinement of Mott’s theory was required. Roberts [118] suggested that for large samples Mott’s assumption that \( D \) extends over the entire sample would result in the system inertia becoming significant. Consequently the terminal velocity of the crack tip will be reduced. Roberts alternative was that the circular region \( D \) should have a radius \( r = vt \) which is the distance travelled by a Rayleigh wave in a time interval \( t \). In the same time
interval the crack tip extends a distance \( dc = v_T t \) where \( v_T \) is the terminal velocity of the crack. Equating these expression we have \( v_R/v_T = v(k/2\pi) \).

Roberts found an alternative expression for the constant \( k \) by numerically evaluating the integral (42). Simultaneously solving the two conditions gives a value \( v_T = 0.38v_R \). Therefore for silica glass we have \( v_T \approx 1.95 \text{km}s^{-1} \).

### 2.5.4 Crack Propagation near Terminal Velocity

The behaviour of a crack changes as it approaches terminal velocity. Considering the energy balance equation (38), once terminal velocity is reached the \( U_K \) term has reached a maximum value. Consequently any additional energy coming into the system must go into the \( U_S \) term. As the \( \gamma \) term is constant the only way for the \( U_S \) to incorporate additional energy is by creating additional surfaces. This is accomplished through crack bifurcation.

Field [117] analysed crack paths in glass microscope slides. The slides contained an initial edge crack and were placed under an increasing tensile load until fracture occurred. The size of the initial edge crack was increased resulting in a decrease of the fracture stress. Field showed that crack bifurcation took place at a prescribed point in each case. This analysis also showed the stress intensity factor at the branching point is constant for a given material.

The mechanism causing bifurcation has been attributed to a variety of dynamic effects. Yoffe [119] and Erdogan [120] analysed steady-state solutions of the equations of motion in an elastic medium. They concluded that at high velocities the stress field at the tip of the propagating crack is distorted by up to \( 70^\circ \) as the crack velocity reaches \( 0.38v_R \). In practice bifurcation takes place at lower velocities than predicted by the theory and the bifurcation angle is more severe [117]. However there is qualitative agreement between theory and experiment. For small scale substrates undergoing fracture stress, waves propagating from the crack tip may reflect off a boundary and return to interfere with the advancing crack. Stress waves can also reflect off inhomogeneities in the material. Interference with the stress field around the crack tip may trigger bifurcation. Tertiary fracture occurring ahead of the crack front has also been suggested as a bifurcation mechanism [117].
2.6 Summary

This review section has discussed the prominent research publications, at the time of writing, in the area of laser glass interactions and brittle fracture. The fundamental principles of laser operation and the propagation of light in transparent materials has also been discusses.
Chapter 3
Materials and Methods

This chapter describes the experimental configurations and materials used in the subsequent results chapters. This includes laser sample processing configurations, characterisation tools and computational modelling software packages. The material properties and relevant manufacturing methods of glass substrates used in experiments are discussed.

3.1 Glass Science

This section describes the theory of formation of glasses. The use of dopants to improve the optical and mechanical properties of glass is examined. Laser scribing of glass is directly affected by the optical and mechanical properties. Historic and relevant current glass manufacturing techniques are discussed.

3.1.1 Glass Transformation Range

A glass is formed by cooling a liquid fast enough to avoid crystallisation. In theory any liquid can form a glass if the cooling rate is high enough [121]. Silica is distinct from other materials in that it can be cooled to form a glass on macro timescales. For a liquid where the timescale of crystallisation of the material is negligible compared with the cooling rate, a discontinuity in the material volume occurs at a particular melting temperature ($T_m$). This marks the point where an atomic rearrangement to a crystal structure takes place (Figure 3.1). For a liquid with a relaxation time comparable to laboratory timescales or cooled fast enough, we have a gradual decrease in volume with no sudden atomic rearrangement. The increasing viscosity with decreasing temperature makes it progressively more difficult for molecules to rearrange. The structure begins to lag behind the equilibrium arrangement which would be reached if sufficient time was allowed. The rate of change of volume with temperature begins to decrease and become nonlinear. This marks the start of the glass transformation region. Eventually with further decreasing temperature the viscosity becomes so great that the atoms cannot move and
the glass is ‘frozen’ in a liquid-like state. The rate of change of volume with temperature becomes linear once more. This marks the end of the glass transformation region. Glass is isotropic and lacks long range order, similar to a liquid. The fundamental distinction between a liquid and a glass is that a glass has a non-zero shear modulus, similar to a solid. Inorganic glasses can form fine grained polycrystalline materials when given a slow high temperature heat treatment, for example silica glass and quartz crystal[3].

![Graph showing volume versus temperature for a crystalline material and a material exhibiting a glass transformation temperature.](image)

Figure 3.1: Volume versus temperature graph for a crystalline material and a material exhibiting a glass transformation temperature.

The ease at which a liquid can form a glass is dependent on the variation of viscosity with temperature. At high temperature the viscosity of a liquid follows the Arrhenius law. At lower temperatures this dependence breaks down and the viscosity is given by an empirically derived law known as the Vogel-Fulcher law [122].

$$\eta = \eta_0 \left[ \frac{B}{T - T_0} \right]$$

(43)

$B$ and $T_0$ are material constants. The mechanism governing glass transformation is an open question in condensed matter physics [122-124]. Two prominent theories are the free volume theory and the cooperativity theory. Free volume theory relates the viscosity of a liquid to the fraction of the liquid volume which is ‘free’ to permit motion of nearby material. The model is in agreement with the Vogel-Fulcher equation only for certain experimental conditions. It fails to predict the behaviour of a polymer forming a glass under varying pressure.
Materials and Methods

Cooperativity attempts to explain the glass transition by relating it to the idea of molecules cooperating and moving out of the way to allow space for another molecule to relax. At higher densities more molecules must cooperate to allow relaxation to take place making the process slower and more difficult.

Many materials aside from oxides exhibit glass transformation behaviour. Chalcogens doped with arsenic and germanium form chalcogenide glasses. Pure sulphur, phosphorus and selenium readily form glasses which are used in niche optical applications. Organic molecules such as glycerol and sucrose can form glasses, best known for use in movie stunts. Most polymers exhibit glass transformation behaviour, polycarbonates are in everyday use in glass form across a wide range of applications. Extremely high cooling rates can be used to form glass out of some metallic alloys, such as copper. Metallic glasses have unique magnetic properties and are used in electric motors, transformers and recording heads[122].

3.1.2 Optical Properties of Glass

Pure silica glass is an insulating material and like other insulating materials silica has a transparency range. The transparency of glass covers the entire visible range, while glass is highly absorbing at UV and IR wavelengths (Figure 3.2). Pure silica based glass is highly transparent in the visible region, the bulk of the attenuation occurring is due to reflection off the front and rear surface of the glass. The amount of light reflected is dependent on the refractive index. The abrupt absorption edge at ~300nm is known as the fundamental absorption edge and is determined by the bandgap of the material. Once the incident photons have sufficient energy to excite a valence electron to the conduction band strong absorption will occur giving the well-defined threshold seen in Figure 3.2. The gradual increase in absorption for λ>2500nm is due to excitation of vibrational modes of the constituent molecules. The various absorption mechanisms of glass are discussed in more detail in section 2.3. CO₂ lasers typically output at a wavelength of 10.6μm making standard silica glass optics unsuitable. CO₂ laser optics are instead made from zinc selenide (ZnSe), a chalcogenide crystalline compound. ZnSe has a low absorption coefficient in the IR region but comes at a higher cost than silica based optics and is toxic.
Figure 3.2: Transmission spectrum for silica glass. The solid blue line represents transmission data measured using a spectrophotometer with 130μm thick borosilicate willow glass. The red dashed line is taken from data published by Drummond [125], which was measured on 5.97mm thick optical quality fused silica. Plots are not normalised for reflection.

The transparency and high refractive index of glass makes it useful in optical elements. Silica glass has a refractive index of 1.51 for optical wavelengths. While this is smaller than diamond materials (~2.5) glass is inexpensive and can be doped to increase the refractive index (see section 3.1.3). The refractive index varies with wavelength. In the visible spectrum the value increases with decreasing wavelength (Figure 3.3). The variation with wavelength is the cause of chromatic aberration in optical systems.
Materials and Methods

Figure 3.3: Plot of experimental measurements of refractive index of SiO$_2$ taken from Palik [17] The results of 15 separate studies are combined to give the above graph. The technique used for measuring the refractive index depends on the wavelength, and include the minimum deviation angle method, interferometric methods and the Kramers-Krönig analysis of reflectance data

3.1.3 Glass Composition

Most types of glass are consist of silica (SiO$_2$) combined with other oxides. Silicon and oxygen form a covalent bond. The basic unit cell for silicates is tetrahedral where each silicon atom is bounded to four oxygen atoms [3]. This arrangement has a net negative charge as each oxygen atom requires an electron to be electronically stable. Silica is the simplest chemical form of silicate materials. Each corner oxygen atom in the tetrahedron is shared with an adjacent tetrahedron. Silica can form crystalline and amorphous structures. There are multiple possible crystalline arrangements of SiO$_2$ tetrahedrons. Three prominent forms are quartz, cristobalite and tridymite. Pure amorphous silica can be transformed to crystalline forms with high temperature heat treatment. Birefringent effects will occur in these crystalline forms due to anisotropy in the structure.

Glass has huge variety in functionality depending on doping. Doping is done by adding the particular oxide dopant to a glass melt mixture. Pyrex glass is doped with B$_2$O$_3$, causing a reduction of 60% in the thermal expansion coefficient. The resulting borosilicate glass product is less likely to fracture when suffering thermal shock making it suitable for temperature
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fluctuating applications however it comes at a higher cost. Soda lime glass is cheap to manufacture and is the most commonly encountered glass in daily life (windows, containers). It is doped with Na₂O, CaO and a small amount of Al₂O₃. The doping lowers the melting temperature of the glass allowing cheaper processing and recycling. Optical glasses are doped with PbO to increase the refractive index and improve optical performance. Dense flint glass is heavily doped with 62% PbO increasing the refractive index to 1.746 and increasing the optical power of such lenses. Depending on doping, a silica based glass can have a refractive index in the range 1.5–2.1 [3], making it flexible for many applications. Lead doping also increases the density of the glass. Doping glass to increase the refractive index comes at the expense of decreasing UV transmission [15].

Table 3.1: Compositions of commonly encountered glass types. Data aggregated from [3, 15]. Values for refractive index is quoted at 546.1nm. Transmission was measured at 310nm for 10mm thick plate.

<table>
<thead>
<tr>
<th>Glass Type</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>B₂O₃</th>
<th>PbO</th>
<th>Other</th>
<th>n</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Silica</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.46</td>
<td>0.91</td>
</tr>
<tr>
<td>Borosilicate</td>
<td>81</td>
<td>3.5</td>
<td>2.5</td>
<td>13</td>
<td></td>
<td></td>
<td>MgO 4</td>
<td>1.47</td>
<td>-</td>
</tr>
<tr>
<td>Soda Lime</td>
<td>74</td>
<td>16</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>1.51</td>
<td>-</td>
</tr>
<tr>
<td>Light Flint</td>
<td>47</td>
<td>5</td>
<td></td>
<td></td>
<td>34</td>
<td></td>
<td>K₂O 8</td>
<td>1.585</td>
<td>0.008</td>
</tr>
<tr>
<td>Dense Flint</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
<td>62</td>
<td></td>
<td>K₂O 5</td>
<td>1.746</td>
<td>0</td>
</tr>
</tbody>
</table>

Coloured glass can be produced by doping with semiconductors with band gaps in the visible spectrum. The dopants will absorb only certain parts of the visible spectrum altering the transmission of the glass and giving it a coloured appearance. The colour perceived is a combination of the wavelengths transmitted. The colour of the glass is dependent on the dopant concentration and so can be tuned. A ruby crystal consists of sapphire doped with Cr³⁺ ions. The chromium ions has two absorption bands in the blue and green wavelengths [3]. The net effect is a red colour in the crystal. In some cases where the dopant crystals are similar in size to the electron wavelength we have a quantum size effect occurring. The electron energy will be increased shifting the band gap towards the UV [15].

When producing glass the particular components required to give the desired performance are mixed into a melt. The melt is homogenised by mechanical stirring and convection currents. Time must be allowed for gas bubbles and inclusions in the mixture to be absorbed or rise to the surface where they can escape.
3.1.4 Glass Manufacturing

Glass containers and instruments were originally hand blown. Air was forced into molten glass on the end of a pipe by blowing into it. This forms a hollow in the glass. The glass was rotated and shaped using wooden instruments until the desired shape was achieved. The process can be automated by forcing molten glass into a mould followed by compressed air to fit the glass to the mould contours. Glassware and light bulbs are manufactured using this process. Flat glass can be manufactured by rapidly spinning the molten glass until it is flattened by centripetal force. The glass is not completely flat and is slightly thicker in the middle. The point where the blowing pipe connected to the molten glass leaves behind a protrusion which was sometimes used as a rudimentary lens [4]. The hand blowing process is time-consuming with varying quality in the finished products.

Initial techniques for mass production of flat glass involved casting molten glass on a metallic table and rolling between metal rollers. The rollers were cooled to cause solidification of the glass on contact. As the rollers come into contact with the glass in a molten state any surface imperfections are imprinted into the glass causing flaws and non-uniformity in the thickness. Depending on the application, post processing polishing and grinding is required to bring the flatness and quality of the glass to an acceptable level [4]. An improvement on this technique is the float process [126]. Here the glass melt is flowed into a bath containing a molten metal with a lower melting temperature and higher density than the glass so that the glass floats on and is cooled by the metal. The molten metal must also be inert to the molten glass and the ambient atmosphere to prevent reaction products forming or oxidation occurring. Tin and lead fulfil these requirements, however toxic fumes produced by molten lead make tin more suitable for the process despite the higher raw material cost. An atmosphere of nitrogen is maintained over the molten tin to reduce oxidation. The molten glass begins to cool on contact with the molten tin on one side and air on the other. Therefore both sides are free from surface flaws and will be perfectly flat due to surface tension and gravitational forces. The surface exposed to the molten tin will have some diffusion of tin atoms into the melt. Consequently the finished product will have an asymmetric concentration of tin atoms. After sufficient cooling the glass is drawn out of the bath by rollers. Glass thickness is determined by the flow rate of the molten glass into the bath and the draw rate of the rollers out of the bath. Most thick flat glass is produced using the float process.
This study is concerned mainly with laser scribing of ultrathin glass substrates. Ultrathin glass is produced using the overflow and down draw method [127]. Molten glass is flowed at a steady rate into a trough causing the molten material to overflow along both edges (Figure 3.4). For a flat trough the flow rate over the edge would decrease along the edge resulting in non-uniformities in the process. To prevent this the depth of the trough is specially tapered along its length to achieve an even overflow rate. The trough must be inert to the molten glass and able to withstand significant mechanical strain and temperature gradients. Troughs are typically manufactured from zircon to meet this requirement [128]. The glass flows along the sides of the trough to the bottom where it meets the glass flowing from the opposite edge. The streams fuse into a single sheet which then flows downwards under the force of gravity. The glass surface is free from flaws as it does not contact any solid surfaces after fusing. The bottom of the trough is specially shaped to promote flow of the fused glass downwards. A drawing mechanism is used to draw the newly formed glass sheet away from the trough at a steady rate. The drawing rate determines the thickness of the glass sheet. Typically mechanical rollers are used. The drawing mechanism is located far enough downstream from the overflow apparatus that the glass has cooled and solidified before coming into contact with the roller. The rate of cooling of the overflowed glass must be carefully controlled to prevent non-uniformities in the glass thickness due to the strong temperature dependence of viscosity [129]. The key advantage of this technique is that the molten glass which ends up forming the outer surface of the glass sheet does not come into contact with any part of the apparatus before it cools. This reduces defects and impurities in the final product. The molten glass which is in contact with the trough is fused into the bulk of the glass sheet and so is of less importance. Using this technique glass as 100µm thick has been mass produced [130]. The processing speed of the overflow process is lower than the float process and so it is only used for specialist applications.
Optical fibres are manufactured using a preform method. The cladding is produced by flowing a melt through an orifice, the centre of which is partially blocked by a bell shaped blowpipe. Air flow through the blowpipe will produce the hollow cladding. Without airflow the inner core of the glass can be formed. The core is placed inside the cladding and heated to fuse the components together. Fibres for telecommunication purposes are made from high purity vitreous silica. Fibres produced from melts will be of insufficient quality. The core is formed inside the cladding in a vapour deposition process. The deposition occurs inside the heated cladding. Since the glass never contacts any crucible high purity is maintained [4].

After production any residual stresses present in the glass must be thermally annealed. The glass is loaded into a high temperature oven, called a lehr. The oven is set to a temperature in the glass transformation range of the sample. The sample is held at a uniform and constant level until sufficient stress removal has taken place. As glass is transparent stresses in the glass can be viewed directly with crossed polarisers, due to photoelastic effect. After treatment the glass must be cooled slowly and uniformly to prevent further stresses developing in the glass.

As discussed in section 2.5.1 the fracture strength of glass is significantly reduced by naturally occurring stress raisers. Increasing the fracture strength of glass is of huge interest to
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glass manufacturing companies in applications where the glass is load bearing or subject to mechanical shock. Techniques to reduce the size and density of stress raisers formed in the glass during production have been developed. These techniques include flame polishing, chemical etching. Flame polishing eliminates flaws in the surface of the glass by heating the surface of the glass to its melting temperature. The molten glass will flow due to surface tension and fill any flaws in the surface and the glass is cooled. Chemical etching lowers the stress concentration factor of the flaws by reducing flaw length and blunting the tip. Removal of flaws is only a temporary solution as fresh flaws will begin to form once the glass is exposed to atmospheric conditions [4]. Lubricants and coatings can be applied to the fresh glass surface to reduce the coefficient of friction and suppress the formation of surface flaws [4].

Fracture in glass occurs when surface flaws are activated by tensile stress due to their stress raising properties. Rather than remove the flaws it is feasible to increase the fracture strength by establishing a residual compressive stress in the surface of the glass. When a tensile load is applied to the glass the net tensile stress will be reduced giving a higher fracture strength. Deliberately establishing a residual stress in a glass substrate is known as tempering. In glass manufacture there are two types of tempering; thermal and chemical. Thermal tempering is carried out by rapidly and uniformly cooling a glass substrate which has been heated to just below the softening point. Air jets are used to provide the cooling. The bulk of the glass substrate will cool more slowly than the surface region. The surface region will try to compress, but is unable to do so as it is bound to the bulk warmer part of the substrate. Because of this the surface region will have a residual compressive stress while the bulk of the glass will have a tensile stress. Thermal tempering is ineffective for thin glass substrates and for glasses with a low thermal expansion coefficient. An example of acute thermal tempering is a Prince Rupert drop [131]. Prince Rupert drops are formed by dripping a small amount of molten glass into a volume of cold water. The glass will rapidly cool forming oblong teardrop shaped solid. The inner part of the drop will cool more slowly than the outer layer initiating thermal tempering. When the structure has reached thermal equilibrium there are large compressive and tensile stresses in outer and inner layers respectively. Due to the large compressive stresses the ‘head’ of the drop exhibits remarkable fracture strength and can withstand hammer blows without fracture. The narrow tail of the drop is too thin to for effective tempering to occur and so will fracture with little applied stress. When the drop fractures the internally stored potential energy is rapidly released causing explosive fracture of the drop into small granular pieces.
Chemical tempering is carried out by exchanging sodium ions in the glass surface with larger potassium ions. The difference in volume between the two ions causes a compressive stress in the glass surface. Ion exchange is carried by submerging the glass substrate in a molten salt bath. ‘Gorilla’ glass is a commonly encountered chemically tempered glass produced by Corning. It is difficult to chemically temper soda lime glass as the glass transformation temperature of soda lime glass is comparable to the temperature of the salt bath and so unintentional annealing will take place [4].

Fractured tempered glass will form small granular chunks due to the strong tensile stress in the bulk of the glass. This is in contrast with untempered glass which will form large shards. Consequently tempered glass is used in situations where fractured untempered glass would be likely to cause injury, such as car windscreens. The tensile stress layer in chemically tempered glass is used in some laser cutting processes to assist in the cleaving of glass. The scribed glass will self-cleave after a time delay [98]. The self-cleaving step reduces the complexity of the glass scribing process.

Fusing a surface layer with a lower thermal expansion coefficient to the bulk glass will result in compressive surface stresses when the substrate is cooled. A similar effect is possible using an alternative ion exchange process designed to lower the thermal expansion coefficient of the glass surface. Glass submerged in a lithium ion bath will have a lower thermal expansion coefficient in the surface exchange regions only, making it less susceptible to thermal shock. The glass transformation temperature of the glass must be similar to the temperature of the bath to allow stresses from the ion exchange to relax [4].

3.2 Laser Processing Systems

This section describes the operation of the lasers used in glass scribing experiments along with focusing optics, sample placement and beam delivery systems.

3.2.1 FS Laser

The ultrashort laser used for glass processing was an Amplitude systems s-pulse laser. The laser head contains the laser oscillator, a pulse chirper, an optical routing device and a regenerative amplifier. The outputted beam then travels through an interface box where power
attenuation and harmonic generation are performed. The output of the interface box is directed by mirrors across the optical table to the sample processing area.

The active laser material in the oscillator is a ytterbium doped crystal (Yb:YKW) inside a Fabry-Pérot cavity. Triply ionised ytterbium ions are highly absorbing in the 940 – 980nm range. The medium is pumped by diode lasers with an output wavelength overlapping with the absorption range of the doped crystal. The fluorescence bandwidth is sufficiently large to sustain ultrashort pulse generation. The laser oscillator outputs linearly polarised laser pulses with a <20nJ energy at a repetition rate of 30MHz and a pulse duration of 200fs.

The pulse is first directed towards the pulse stretcher. Amplifying a pulse this short is not feasible as the high intensities give rise to self-focusing which will damage the amplifier crystal. To avoid this the pulse is temporally stretched by a pair of dispersion gratings in a process referred to as chirped pulse amplification (see section 2.2). The chirped pulse is then directed towards the regenerative amplifier. The pulse is trapped inside the amplifier by polarisation dependent reflections. A Pockels cell rotates the plane of polarisation of the beam so that it will be transmitted through a Brewster window and make a trip around the amplifier and back to the Pockels cell once again. A Pockels cell is essentially a rapidly variable half waveplate which makes use of electro-optic effects to produce birefringence in a crystal material with nanosecond scale response time. The amplifier uses an Yb:YKW crystal as the laser medium, identical to the laser oscillator crystal. The crystal is strongly pumped using diode lasers to increase the gain coefficient and amplify the signal. The pulse makes successive trips around the amplifier until a desired energy level has been reached. Once this occurs the Pockels cell will rotate the plane of polarisation once again and the beam will reflect off the Brewster window and out of the amplifier.

A Faraday rotator and another Brewster window is used on the amplified pulse to direct it towards the pulse compressor. This prevents the beam reflecting back to the pulse stretcher. A Faraday rotator rotates the plane of polarisation non-reciprocally and so only light exiting the amplifier will be effected. At the pulse compressor a second pair of gratings undo the pulse stretching. The pulse is compressed temporally to 500fs. The dispersion gratings are mounted on high precision linear motors which can be externally controlled to vary the pulse duration of the outputted pulse. The amount of compression is dependent on the separation between the gratings and so by moving the gratings the pulse duration can be controlled. The pulse duration
can be varied from 500fs to 10ps. After compression the pulse is directed out of the laser head towards the interface box.

| Table 3.2: Specifications for Amplitude Spulse laser. |
|---------------------------------|----------------|
| Wavelength                      | 1030nm         |
| Repetition Rate                 | 1-300kHz       |
| Maximum Power (10kHz)           | 3.2W           |
| Pulse Duration                  | 0.5-10ps       |
| Raw Beam Diameter               | X=2.34mm, Y=2.12mm |
| Focused Spot Diameter (1/e²)    | 59.7µm         |
| M²                              | 1.2            |

Heat generated in the laser crystal, laser diodes and Pockels cell is dissipated by a water cooling system. The chiller unit is separate to the laser head and houses a heat exchange unit and a water pump. The cooled water is pumped in a loop through 8mm diameter hosing around the laser head. The laser temperature is monitored by the chiller and precisely maintained at 24°C. A flow rate of ~2.8l/min is required to cool the laser sufficiently. The chiller uses distilled water with 10% optishield 2 concentration to prevent limescale and organism growth.

Figure 3.5: Visual representation of the ultrashort pulse production inside the spulse laser head. The insert diagram shows the laser amplifier design. Note the abbreviations used: Faraday rotator (FR), Pockels cell (PC).
The interface box contains a variable laser attenuator and harmonic generation crystals. The incoming laser beam is first incident on the attenuator. The laser attenuator consists of a motorised half waveplate and a Brewster window. The half waveplate is rotated with an external switch causing the plane of polarisation of the laser to rotate at twice the angle. If the plane of polarisation of the laser is perpendicular to the transmission axis of the Brewster window then the transmitted power is zero. The transmitted power will be maximum if the laser is polarised parallel to the transmission axis. The attenuation can be fully scaled depending on the mismatch between the two. The laser power reflected from the Brewster window is directed to a lithium triborate (LBO) second harmonic generation crystal. The pulse is frequency doubled to a wavelength of 515nm. A manual flip mirror is used to direct the beam to a barium borate (BBO) third harmonic generation crystal for an output wavelength of 343nm. There are significant energy losses associated with harmonic generation process. The process is most efficient at low repetition rates, at 1kHz the second harmonic generation is 66% efficient while the third harmonic generation is 31% efficient. At 100kHz this drops to 15% and 11% for the second and third harmonic generation respectively.

The laser beam then exits the interface box and is directed across the optical table towards the sample processing station. An optional beam path is available to direct the beam through a variable beam expander. The path is selected by a manual flip mirror. The beam expander is designed for IR and green wavelengths and has magnifications from 1.5x to 5x. Another optional beam path directs the beam towards an auto correlator which can be used to measure the pulse duration (Figure 3.6). The correlator unit comprises a Michelson interferometer, a second harmonic generation crystal and a detector. The beam is incident first on the interferometer where it is split into two beams and sent along the two reflecting arms of the interferometer. One of the mirrors in the interferometer is continuously moving in and out with respect to the beam. The beams are recombined in the splitter and focused onto a second harmonic generation crystal. Light generated in the crystal is detected and the intensity of the light can be correlated with the phase difference and pulse duration of the two beams.
Figure 3.6: Measured pulse duration of IR beam from spulse laser. The data is averaged over 16 readings to minimise noise.

Samples are placed on a stainless steel sample stage which is itself mounted on linear motion stages (Aerotech) to allow CNC XYZ movement (Figure 3.7). Movement in the XY direction is achieved by two linear ABL100 stages. Each stage moves along a single axis however one is mounted perpendicularly on the other allowing biaxial movement. Vertical movement in the Z direction is controlled by an AVL125 vertical translation stage which is mounted onto the ABL100 stages. ABL100 linear motion stages have a max movement speed of 500mm/s with a positional accuracy of 0.5μm. AVL125 vertical translation stages have maximum movement speed of 100mm/s with a positional accuracy of 1μm. The stages are controlled by a A3200 npaq control unit. The A3200 is connected to the external laser trigger allowing synchronous control of stage movement and laser switching. The user controls and programmes the stages using NView PC software.
Figure 3.7: Typical sample processing setup for spulse FS laser using galvo scanner.

3.2.2 **NS Laser**

The laser used for glass processing was a Spectra-Physics high peak power oscillator (HIPPO) laser. The laser head houses a neodymium-doped yttrium orthovanadate crystal (Nd:YVO₄) as the gain medium. The lasing action is due to the Nd³⁺ ions in the crystal. Due to the wide use of neodymium ions as a dopant in laser gain mediums, properties of such doped crystals have been comprehensively studied. The energy level diagram of triply ionised neodymium ions consists of four levels and has absorption bands in the red and infrared. Electrons are excited to the E₄ level which has a short lifetime and so quickly relax in a radiationless transition to the E₃ level. The E₃ level has a lifetime of approximately 100µs allowing time for population inversion to take place between the E₃ and E₂ levels[132]. This results in a stimulated emission at 1064nm. Other competing spontaneous emissions are suppressed by wavelength filtering optics.

The gain medium is pumped by two FCbar diode lasers devices emitting at 808nm which strongly overlaps with the Nd³⁺ absorption band with minimal thermal loading. Each FCbar contains 19 emitters. The diode lasers are housed separately in the power supply and are coupled to the gain medium by optical fibre bundles. Fibres are coupled to individual diodes in the laser diode bar and then brought together into a tightly packed round bundle. The crystal
is pumped until the pulse energy reaches a prescribed level and the resonant cavity is rapidly Q-switched to release the pulse. The power supply is fan cooled and maintains the diodes at their optimum operating temperature. Vanadate gain mediums suffer from thermal lensing effects caused by temperature gradients inside the crystal. To minimise this the HIPPO laser uses a patented resonator design where the gain medium is end pumped by the focused laser diodes. A water chiller is used to dissipate heat generated in the laser head. The chiller is separate to the laser head and pumps water around in a closed loop. The chiller monitors the laser head temperature and maintains it at 20°C. The beam exiting the laser head is sampled using a beam splitter and a photodiode to determine the power level of the beam. Only a small portion of the beam power is sampled and the photodiode is calibrated to determine the power in the actual beam.

A harmonic module can be bolted to the laser head to achieve 355nm output. The harmonic module contains a LBO frequency tripling crystal to convert from 1064nm light to 355nm. The conversion efficiency of the crystal is dependent on the repetition rate and crystal temperature. At 30kHz the conversion efficiency is 32% and drops to 5% at 300kHz. The HIPPO laser software also allows the user to tune the crystal temperature for optimum performance. The harmonic crystal is mounted on a micro-positioning stage allowing control over the orientation of the harmonic crystal.

Table 3.3: Specification for Spectra Physics HIPPO laser

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>1064nm</th>
<th>355nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>17W at 30kHz</td>
<td>5.5W at 30kHz</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>15-300kHz</td>
<td>15-300kHz</td>
</tr>
<tr>
<td>Pulse Duration</td>
<td>15ns</td>
<td>13ns</td>
</tr>
<tr>
<td>M²</td>
<td>&lt;1.2</td>
<td>&lt;1.3</td>
</tr>
<tr>
<td>Raw Beam Diameter</td>
<td>0.6mm</td>
<td>1mm</td>
</tr>
<tr>
<td>Focused Spot Diameter (1/e²)</td>
<td>37.8µm</td>
<td>16.4 µm</td>
</tr>
</tbody>
</table>

After exiting the harmonic head the laser is directed across the optical table by mirrors. A power meter (Ophir) can be used to directly measure beam power. The sample processing station has a gantry arrangement where the focusing lens is above the sample in a vertical arrangement. The beam is directed up and across the gantry. Typically a galvo scanner (scanlab) with a f=100mm Ftheta focusing lens is used to focus and scan the laser. The galvo scanner is controlled and programmed using winlase PC software. The sample stage is mounted
on a ball screw drive linear translation stage (Aerotech ATS100). The stage is controlled using nview PC software and has a positioning accuracy of 1µm with a maximum speed of 70mm/s. The stage is mounted vertically to translate the sample in the z plane. Position in the xy plane can be affected by manual screw stages (Figure 3.8).

![Figure 3.8: Typical sample processing setup for HIPPO ns laser using galvo scanner.](image)

### 3.2.3 CO₂ Laser

The laser used for glass processing was a Coherent diamond Gem-60 CO₂ laser. CO₂ lasers achieve lasing action by exciting vibrational modes in the carbon dioxide molecules rather than electronic modes. The three basic vibrational modes are symmetric, axisymmetric, and bending. The axisymmetric vibrational is the highest energy state. The gaseous laser medium is excited by radio frequencies into vibrational states. An excited axisymmetrically vibrating molecule can undergo spontaneous emission of a photon and relaxation to a symmetrically vibrating mode. If the emitted photon is parallel to the optical axis of the resonator then it will oscillate through the gain medium. The photon may encounter another axisymmetrically excited molecule and cause stimulated emission to occur. The emitted photon will be in phase and travelling the same direction as the stimulating photon. The rate of spontaneous emission from the symmetrically vibrating mode is higher than the axisymmetrically vibrating mode and so
with continued radio frequency pumping a population inversion will occur and lasing is sustainable.

The distinguishing feature of CO₂ lasers is the high power and energy efficient output. This is facilitated by a mixture of nitrogen gas in the laser medium. Nitrogen gas supports only one vibrational mode and cannot emit photons due to its homogeneous structure. The excited vibrational mode has a long lifetime. The energy of this vibrational mode is a good match to the energy required to excite a CO₂ molecule into an axisymmetrically vibrating mode. Thus unexcited CO₂ molecules can be excited through collisional excitation with excited nitrogen molecules greatly increasing the population inversion and gain coefficient.

The efficiency of this excitation is dependent on the gas temperature and so cooling of the laser medium is an important consideration. The laser medium is made up of 78% helium 13% nitrogen and 10% carbon dioxide. The helium is used for its favourable thermal conduction properties. The laser head is cooled by a water cooling unit. The unit is separate to the laser head. Water is cooled in the unit and pumped around the laser head in a closed loop at a rate of 6l/min. The laser is pulsed by an external pulse generator. The power is varied by changing the duration of the pulse and the repetition rate, with longer pulses and higher repetition rates having higher power.

Table 3.4: Specification for coherent Gem-60 CO₂ laser.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wavelength</strong></td>
<td>10.6µm</td>
</tr>
<tr>
<td><strong>Power</strong></td>
<td>50W at 25kHz</td>
</tr>
<tr>
<td><strong>Repetition Rate Range</strong></td>
<td>0.1-25kHz</td>
</tr>
<tr>
<td><strong>Pulse Duration</strong></td>
<td>10-100µs</td>
</tr>
<tr>
<td><strong>M²</strong></td>
<td>&lt;1.3</td>
</tr>
<tr>
<td><strong>Raw Beam Diameter</strong></td>
<td>3.8mm</td>
</tr>
<tr>
<td><strong>Focused Spot Diameter (1/e²)</strong></td>
<td>39.4µm (calculated)</td>
</tr>
</tbody>
</table>

After exiting the laser head the beam is directed through a lens tube and turned 90° by a mirror into another lens tube which contains the focusing optics (Figure 3.9). The objective lens was a 38mm focal length ZnSe meniscus lens. The focal plane is varied by adjusting the height of the laser and lens tube configuration using a vertical lift stage. A coaxial air nozzle is fixed to the end of the lens tube. Compressed air can be propelled through the nozzle onto the sample to remove debris and to prevent material vapour depositing on the lens. The width of the nozzle is sufficiently large to prevent clipping of the laser beam. The sample is mounted on
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an XY movement stage (aerotech). The stage is controlled using the nview PC software. The laser is scanned by moving the stage relative to the stationary laser beam. When necessary the sample was cooled by a cool air jet emitted from a compressed air vortex cooler (Meech). The cooler emitted an air jet with a temperature of approximately -5°C. Laser power can be measured after the objective lens using a power meter (thorlabs). Power is measured out of the focal plane to prevent damage to the instrument. The power was varied by adjusting the pulse duration of the signal generator triggering the laser.

![Diagram](image)

Figure 3.9: Typical sample processing setup for GEM60 CO₂ laser.

3.3 Experimental Techniques

This section outlines some of the relevant techniques for processing samples and analysing results.

3.3.1 Beam Delivery

For sample processing the beam is directed up and across gantry where focusing optics are used to focus the beam on the sample processing stage below in a vertical arrangement. A power meter (Ophir) is placed immediately before the focusing optics to measure the laser power. Two alternate focusing arrangements are used in this work: a galvo scanner with an F-
theta lens and a fixed lens on an optical rail. A galvo scanner consisted of two internal mirrors capable of rapid and precise CNC movement. Focusing of the beam is achieved by an F-theta lens (Linos F-theta ronar). The lens had a focal length of 100mm and a NA of 0.71. An F-theta lens is a specially designed lens which has a flat focal plane regardless of the deflection of the incident beam. This is useful when using galvo mirrors to scan a laser beam as the focus will not change across the scan range. The galvo is controlled using winlase PC software. The winlase software is connected to the laser external trigger and so can synchronise the movements of the mirrors with the laser gating.

Where fixed focusing optics are required an optical rail setup is used. The rail consisted of a mirror and a focusing optic. The mirror directed the beam downwards through the focusing optic and onto the sample. Care must be taken to ensure there is good vertical alignment along the rail. Scanning of the laser in this case is achieved by moving the sample relative to the laser using a linear motion stage.

The beam waist ($\omega_0$) of a focused Gaussian laser beam with $1/e^2$ raw beam radius $a$ occurs at the focal length ($f$) of the lens and can be approximated from the formula (44) [42].

$$\omega_0 = \sqrt{\frac{2f\lambda}{\pi a}} \quad (44)$$

This formula assumes the divergence of the beam is negligible. This formula becomes increasingly inaccurate for high NA focusing optics. It is possible to directly measure the beam waist using a beam profiler to measure the beam waist and scanning through the focal range to find the minimum value. This method is time consuming and difficult to carry out for tightly focused laser spots, due to the risk of the high laser fluence damaging the instrument. An alternative in situ technique for measuring the beam waist, referred to as Liu’s method[133], was also used. A series of craters are ablated on a flat substrate by a focused laser beam with varying pulse energies. The diameter of each crater can be easily measured using an optical microscope. The relationship between the spot diameter ($D$), the pulse energy ($E_p$) and the beam waist is given by:

$$D^2 = 2\omega_0^2 \ln E_p \quad (45)$$

By plotting the square of the crater diameter against the natural log of the pulse energy the beam waist can be determined from the slope of the plot. This gives a simple and precise measurement of the beam waist. This method is most accurate when fluences just above the damage threshold of the material are used. Laser spot sizes quoted in the experimental chapters
were determined using this method unless otherwise stated. Laser spot sizes of defocused beams can also be determined using this method.

The variation of the focused spot size with distance $z$ from the focal plane is given by (46). $z_R$ refers to the Rayleigh length and is given by $z_R = \pi \omega_0^2 / \lambda$. This defines the distance from the beam waist where the diameter of the focused beam has increased by a factor of $\sqrt{2}$.

$$\omega_z = \omega_0 \left[ 1 + \left( \frac{z}{z_R} \right)^2 \right]^{1/2} \quad (46)$$

Tightly focused lasers or UV wavelength beams will have smaller Rayleigh lengths. This adds extra complexity to glass scribing experiments, as care must be taken to ensure the laser focus position is precisely determined and the sample is flat.

### 3.3.2 Elliptical Spot Rotation

Some experiments required an elliptical focused spot shape. When rotation of the spot on the sample is required the sample can be rotated relative to the spot or the focusing optics can be rotated. It is generally simpler to rotate the focusing optics. Attaching the optic mount to a CNC rotary stage, using a threaded mount and an adapter ring, allows synchronous control of the rotation and the laser triggering. An Aerotech MPS-GR50 rotary stage was used. The stage is controlled and programmed using the NView PC software.

### 3.3.3 Polarisation Control

The femtosecond laser used in this study outputs a linearly polarised beam. To alter the orientation of the polarisation relative to the sample a half wave plate can be used to rotate the laser polarisation. The waveplate was mounted in a manual rotary mount in the beam path prior to the objective lens. A waveplate is an optical device which alters the polarisation state of light passing through it. Waveplates are typically constructed out of birefringent quartz for which the refractive index is dependent on the polarisation and propagation direction. This variation in refractive index causes a phase shift between two perpendicular polarisation components of the light wave. The amount of phase shift ($\phi$) depends on the crystal thickness ($L$), the wavelength of light ($\lambda_0$) and the birefringence ($\Delta n$) (47).
\[ \Gamma = \frac{2\pi \Delta n L}{\lambda_0} \] \hspace{1cm} (47)

To convert from linear polarisation to circular a quarter waveplate was used. For a half wave plate the phase shift is equal to \( \pi \). For a quarter wave plate the phase shift is equal to \( \pi/2 \).

### 3.3.4 Sample Cross Sectioning

For high aspect ratio features measuring feature depth using standard techniques was challenging. To characterise the depths a cross sectioning technique was developed (Figure 3.10). The glass sample is scribed with the laser at a specific setting. The sample is then turned over and scribed, at a low power, on the rear surface perpendicular to the first scribe. Mechanical force is used to fracture the sample along the rear side scribe. The sample is then cleaned and mounted onto an angled stub with a carbon tab. This allows the cross section to be viewed directly on a SEM or optical microscope. For SEM imaging a thin gold sputter coating (~40 nm) was required for some samples to reduce charging and improve image contrast.

![Sample Cross Sectioning Diagram](image)

**Figure 3.10: Illustration of sample cross sectioning technique.**

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3.3.5 Mechanical Glass Cutting

An automated mechanical glass cutting workstation was used to mechanically cut thin glass. A sintered carbide cutting wheel was used (Bohle cutmaster platinum). The wheel had a serrated edge which created perforation along the surface of the glass. The wheel holder was on a sliding rail which was free to move in the vertical plane, the applied load on the wheel was then determined by mounting weights onto the holder. The wheel was attached to two linear motion stages (Heiz). One stage was aligned in the X direction and one in the Y direction allowing full XY movement of the wheel across the workpiece. A smaller vertical lift stage was used to position the wheel on the surface of the glass. All the stages are controlled synchronously from a PC using aerotech NView software. The scribing speed was set in the software. An off axis camera was used for precise alignment of the wheel. The sample was held in place using a vacuum stage. The wheel holder could be rotated by 90° using a pneumatic rotator. This allowed scribing in the X and Y direction.

![Photograph of the mechanical cutting workstation used for mechanical cutting of thin glass.](image)

3.3.6 HF Etching

When ablating a transparent material a considerable amount of the laser energy is transmitted through the substrate, depending on laser parameters. This energy does not contribute to the material removal process. To harness this otherwise wasted energy a HF etching technique was
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developed. A HF donor polymer (PVDF) was placed beneath the glass sample. A second glass substrate was placed beneath the polymer to confine the HF acid vapour.

HF gas is produced during thermal decomposition of a polyvinylidene fluoride (PVDF) polymer. The chemical formula of PVDF is \(-(C_2H_2F_2)_n\)-. PVDF has a low melting and boiling point of 160-170°C and. Rapid heating using a laser will produce gaseous HF acid, which will etch a glass material with the chemical reaction \(4\text{HF} + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}\).

![Illustration of rear surface HF etching method. The laser pulse scribes the front surface. Any energy transmitted through the substrate will breakdown the PVDF releasing HF gas which will attack the rear surface assisting in the cutting process.](image)

0.25mm PVDF material (goodfellow) was used in experiments. The release of acidic vapour after ultrashort laser interaction was confirmed with a litmus paper test. The litmus paper was placed in contact with PVDF during laser exposure and turned a dark red colour, indicating a Ph of ~2. More precise Ph measurements were challenging to obtain due to issues containing the acidic vapour. HF gas is an acute poison which interferes with body calcium metabolism. To prevent exposure a strong extract was setup around the sample stage. Appropriate personal protective equipment was used.
3.3.7 Weibull Failure Analysis

Weibull statistical analysis can be used to estimate the probability of failure of a particular part or device by fitting a statistical distribution to a representative empirical data of units which have failed. The Weibull distribution is useful because it is a two parameter distribution and can fit many kinds of data. In this case the Weibull distribution is used to calculate the probability of failure of a laser processed sample under an applied stress $x$. The cumulative Weibull distribution is given by (48)[134].

$$F(x) = 1 - e^{-\left(\frac{x}{\alpha_w}\right)^{\beta_w}}$$  \hspace{1cm} (48)

$\alpha_w$ is the scale parameter and $\beta_w$ is the shape parameter. These values can be determined from a plot of (48). The expression must first be rewritten in linear form(49).

$$\ln\left(\ln\left(\frac{1}{1 - F(x)}\right)\right) = \beta \ln x - \beta \ln \alpha$$  \hspace{1cm} (49)

Analysis by Nelson [135] showed that an empirical plot of $F(x)$ can be produced using $F=(i-0.3)/(n+0.4)$ where $i$ is the rank of the data point in the set and $n$ is the total number of data points. Inserting this expression into (49) and plotting as $y=mx+c$ allows $\alpha$ and $\beta$ to be determined. $\beta$ will be equal to the slope, $\alpha$ will be equal to the exponential of the intercept divided by the slope. Once the $\alpha$ and $\beta$ parameters have been determined the Weibull cumulative distribution function (48) can be used to determine the failure probability at a particular applied stress. A common metric for comparing sample groups is the stress at which 10% of samples will fail at. The error in the estimated value is taken as the standard error: $(\sigma_{std}/\sqrt{n})$ where $\sigma_{std}$ is the standard deviation of the sample and $n$ is the number of data points.

3.3.8 Laboratory Conditions

FS laser experiments, NS laser experiments, SEM analysis and optical microscope analysis were carried out in an ISO Class 7 clean room. Clean room environments limit the number of airborne contaminates. The ISO requirements for a class 7 clean room are that the number of particles greater than 0.5 μm in size must be limited to 352,000 m$^{-3}$ and the number of particles greater than 5 μm in size is limited to 2930 m$^{-3}$. ISO 7 is equivalent to FED STD Class 10000. Incoming air is pumped through filters to limit particulate entering the room. The airflow maintains a positive pressure in the room preventing unfiltered air entering through other means. Users enter the clean room through an intermediate gowning room, where lab coats and
shoe covers are applied limiting contaminations being introduced. A step over bench system is used where a user must be fully gowned before stepping over a barrier to enter the clean room. Particle emitting materials such as paper and certain fabrics are not permitted in the clean room. All surfaces and the floor are regularly wiped down to remove particulate which has settled. The floor has curved edges to facilitate mopping.

For the NS and FS laser configurations the laser, sample stage and all elements in the beam path are mounted on a damped optical table (Newport RS4000). The optical table is supported by pneumatic vibration isolating legs (Newport I-2000) which level the table to an accuracy of 0.3mm and dampen any vibrations.

### 3.3.9 Solenoid Valve Glass Resonance

After laser scribing a mechanical stress can be applied to the substrate to initiate fracture and complete the cut. For thicker glass substrates a chopper bar is typically used to apply a force to the substrate. This method is less suitable for thin glass as the glass is inherently flexible and fragile in nature. A mechanical resonance apparatus was designed to produce a bending stress in glass in a non-contact and easily automated technique.

The apparatus was designed to intermittently release a jet of air onto the sample at a precise frequency. The sample was fixed at both ends and so will oscillate with maximum amplitude if the frequency of the air matches the natural vibrational frequency of the glass beam. The valve used was an SMC SX10 series high speed 2 port solenoid valve. A solenoid valve is an electromechanically operated valve. The solenoid produces a magnetic field when a current flows through it. The magnetic field will lift an internal coaxial plunger, opening the valve. When the current shuts off the magnetic field dissipates and the plunger falls back down, closing the valve. A high 24V TTL signal was used to open the valve and a low signal was used to close the valve. The signal was produced in a signal generator (Thurlby Thandar TG210 2MHz function generator). The valve had a response time of 1.54ms giving a maximum switching frequency (opening and closing) of 325Hz. The output of the signal generator was sampled by an oscilloscope (Tektronix TDS210) as it was found the output of the signal generator was ~50% lower than indicated on the signal generator dial. The valve switched a compressed air supply, and was mounted on an aluminium manifold to allow coupling with compressed air pipes. The compressed air was delivered through 6mm plastic piping and the
pressure was controlled prior to the valve by a pressure regulator. The maximum flow rate of the valve was 100L/min. The air was directed from the output of the pipe towards the bottom surface of the sample. A rigid adjustable spine was attached to the outside of the end of the pipe. This allowed the pipe to be firmly clamped and the direction of the output adjusted. The glass substrate was mounted on two level rigid blocks using scotch tape. Figure 3.13 shows the experimental configuration. The oscillations of the glass substrate were observed using high speed photography techniques (see section 3.4.5).

![Diagram of the Solenoid Valve (SV) Glass Resonance Setup](image)

**Figure 3.13: Diagram of the solenoid valve (SV) glass resonance setup.**

### 3.4 Sample Characterisation Systems

An array of techniques have been applied for sample characterisation. Quantitative data was obtained for surface roughness, scribe depth, scribe width, surface morphology and fracture strength. This section discusses the instruments and techniques used to obtain this data.

#### 3.4.1 Optical Microscopy

High resolution visible inspection of samples was carried out using an Olympus BX60M optical microscope. Features well beyond the resolution of the human eye can be viewed quickly. Optical microscopes use visible light and a series of lenses to magnify micron scale
features. A compound microscope has an objective lens for collecting light reflected from the sample and an eyepiece lens for direct viewing of the enlarged sample. The image is also recorded on a CCD camera, with a live feed from the camera displayed on a computer screen. Computer software allows control of the exposure and gain settings of the camera. A range of objective lenses were available from 5x, 10x, 20x, 50x and 100x. Objective lenses are mounted on a rotating wheel to allow for quick changes. For high magnification strong illumination of the sample is required. Illumination is provided by a 12V halogen bulb with a variable brightness control depending on the requirement. Sample positioning is controlled by adjustable XY screws. The focus is adjusted by lowering and raising the objective lens relative to the sample stage. The resolution of an optical microscope is taken as the minimum distance between two objects which can be resolved. Diffraction effects cause the image to become blurred. Consequently closely spaced objects become difficult to distinguish. Diffraction effects are reduced at shorter wavelengths. Abbe’s equation \( d = \frac{\lambda}{2NA} \) defines the resolution limit of an optical microscope with negligible aberrations, where \( NA \) is the numerical aperture of the objective lens. A high magnification microscope objective will have a numerical aperture in the region of 0.70. For 500nm illumination Abbe’s equation gives an optical resolution of 714nm. When higher resolutions for fine sample features are required SEM techniques are used (section 3.4.3).

Aside from bright field illumination the microscope has dark field and cross polarised light illumination capabilities. Dark field microscopy excludes unscattered light from the final image giving an image of light features on a dark background. A beam stop prior to the sample blocks the central part of the beam and an aperture after the sample blocks any light which has not been scattered by the sample. Dark field microscopy is more suited for detecting small surface flaws or changes in refractive index than bright field microscopy. Cross polarised light illumination gives an image with high contrast in regions with varying refractive index or birefringent effects. Randomly polarised light from the bulb is passed through a linear polariser which will only allow light polarised in one direction to pass. The polarised light is then incident on the sample. The reflected light is passed through another linear polariser which has a polarisation axis at 90° to the first polariser. If no change in polarisation takes place due to reflection from the sample no light will pass through the second polariser. Stress in a material causes a change in refractive index due to the photoelastic effect. Cross polarised light can be used to indicate regions of stress in a transparent sample.
3.4.2 Optical Surface Profiler

An optical surface profiler (Zygo OMP-0360C) was used to measure topographical information about a sample surface. Optical surface profilers use white light interferometry techniques to record information about a sample surface. The profiler method is based on the Michelson interferometer principle. The output of a light source is collimated and directed through a beam splitter. The object beam is directed towards the object being analysed where it undergoes reflection back through the beam splitter and into a CCD camera. The reference beam orthogonally reflects off a flat reference surface and is directed back through the beam splitter into a CCD camera. A live feed of the CCD is displayed on a computer screen to allow adjustment of sample position and focusing. If high surface resolution is required a microscope lens can be incorporated into the system to focus the beam onto the sample. Sample position is adjusted using micro positioning screws. The tilt of the sample stage can also be adjusted. Depending on the difference in path length travelled by the object and reference rays, constructive or destructive interference will occur due to phase difference in the wave fronts. Constructive interference will result in a point of high intensity and destructive interference will result in a point with low intensity. We can also have intermediate regions with no interference where the phase difference is zero.
The intensity of each pixel in the CCD is analysed and fourier transformed computationally to determine the path difference and therefore the object height. To build up a full 3D description of the surface a z scan is performed by moving the reference surface or object relative to the beam splitter. The height of the scan is determined by the user, the Zygo profiler has a vertical scan range of 100µm. The sample under inspection was attached to an aluminium SEM stub. The microscope objectives are interchangeable with 5x, 10x and 20x lenses available. For the 20x objective the optical lateral resolution is 0.71µm while the vertical resolution is 0.1nm. The slope limit for a specular surface is 21.8°. Measurement results are displayed on a computer running metropro software. The software determines the surface roughness from the measurements. The software displays the results as a 2D surface with colour scale indicating height. Line graphs of the surface height can be produced by drawing lines through this plot. A 3D model of the surface is also displayed which can be rotated and zoomed.

Surface profilers struggle to measure surfaces with low reflectivity due to the low signal to noise ratio. Gold sputter coaters can be used to deposit thin gold films onto the surface to increase reflectivity. Fine surface features may be obscured by the film. Deep surface features with high aspect ratios are also difficult to image accurately with a profiler. Multiple reflections occur inside the deep feature scattering light in all directions and reducing the reflected signal to the CCD. Other techniques are required to measure the depth of high aspect ratio surface features, such as the cross sectioning technique in section 3.3.2. The advantage of the profiler method is that the process is non-contact and non-destructive to the sample unlike other methods.
Figure 3.15: Surface profiler setup. The instrument is setup on a rubber vibration reducing pad and a granite optical table. The corner insert shows a surface profile of a laser processed glass surface. Height is indicated by the colour scale.

3.4.3 Scanning Electron Microscopy

Scanning electron microscopy techniques are used when sub-optical resolution of features is required. An electron microscope uses a beam of electrons as a source of illumination. The wavelength of an electron can be orders of magnitude lower than typical wavelengths used in optical microscopes. Considering an electron with a kinetic energy of 1eV the De Broglie wavelength is 1.23nm. According to the Rayleigh criterion optical resolution scales linearly with wavelength. Thus electron microscopes have significantly higher resolution compared with optical microscopes.

In a scanning electron microscope electrons emitted from a heated tungsten filament are accelerated by an applied voltage towards the sample. Electromagnetic lenses use magnetic Lorentz forces to focus the beam of electrons on the sample. Incident electrons lose some energy due to elastic or inelastic collisions depending of the composition of the sample. Inelastic collisions result in the emission of an additional low energy electron from the material called a secondary electron. An elastic collision will cause the incident electron to reflect off the surface. A reflected electron is referred to as a backscatter electron. High atomic number elements backscatter electrons more strongly than low atomic number elements and therefore
backscattered electrons give chemical as well as topographical information about the sample. Secondary and backscatter electrons can be detected to provide information on the surface composition and topography. The electron beam only interacts with a small portion of the sample at a time. The beam is raster scanned over the entire surface to build the picture. The detected electron signal is then correlated with the beam position and an image is computed.

For effective SEM imaging samples must be electrically conductive and electrically grounded to prevent build-up of electric charge on the sample surface. For non-metals this is usually achieved by sputter coating a thin layer of a conductive metal on the sample surface. Metal coatings are also efficient emitters of secondary electrons giving a stronger signal to noise ratio. The primary challenge for SEM imaging is that the chamber must be kept in vacuum during imaging as air particles will interfere with the probing electron beam. This restricts the sample size which can be imaged as the sample is limited by the vacuum chamber dimensions. Powders and other small samples must be held in place to avoid being pulled loose during chamber evacuation.

An FEI Phenom SEM was used for sample imaging. The Phenom SEM is a desktop SEM with reduced resolution and features compared to a full size SEM, but with increased speed and ease of use. The resolution limit for this SEM is ~50nm. Sample size is limited to 25mm diameter and 30mm height. The Phenom SEM uses backscattered electrons for image detection. Samples were attached to a variable angle aluminium stub with a carbon tab. A thin gold coating was applied using a quorum technologies K550X sputter coater. The sputter coater operates by bombarding a gold target with Argon atoms, releasing charged gold atoms. An applied voltage between the negative gold target and the positive sample specimen accelerates gold ions towards the sample. The sputtering chamber is held in a vacuum to improve the uniformity of the deposited film. A 40nm thick coating was typically sufficient for high picture quality. Very fine surface features may be obscured by the coating. The minimum thickness for coating is 4nm and the maximum thickness is dependent on coating time. The coated sample is then placed in the sample holder and loaded in the machine. Zoom and panning of the image is computer controlled.
3.4.4 Two Point Bend Test

The strength of processed samples was determined using the two point bend test technique [136]. The processed glass sample was placed between two vertical plates, one of which is moveable (Figure 3.17). As the plates are brought together the sample flexes causing a tensile stress along the top surface and edges. The stress is maximum at the mid length of the sample. Eventually the bend stress will cause the sample to fracture. The failure stress of the sample can be determined by the separation between the plates. For short samples the contact angle between the glass and the plate is also needed to determine the failure stress.

For metals tensile load measurements are straightforward. The sample is held at both ends and an increasing tensile load applied until fracture occurs. To perform the test the sample must be firmly held at both ends, usually with a clamp. Similar tests are difficult in brittle materials. Attempting to clamp glass may cause fracture of the sample or at least introduce microcracks which will weaken the substrate and corrupt the test results. Analytic solutions for the bend stress in an optical fibre were determined by Matthewson et al [137]. The validity of this analysis for testing thin flat substrates was tested by Gulati et al [136]. Gulati applied strain gauges to a glass substrate during bend testing to determine the bend stress. Good agreement
was found between theory and experiment. The maximum stress ($\sigma_{\text{max}}$) occurs at the midpoint of the sample and is given by (50). $E$ is the material elastic modulus, $t$ is sample thickness, $D$ is the plate separation at fracture and $\theta$ is the contact angle at fracture (see Figure 3.17).

$$\sigma_{\text{max}} = 1.198 \left\{ \frac{Et}{(D-t)} \right\} \sqrt{\cos \theta}$$  \hspace{1cm} (50)

Ideally a stepper motor would be used to bring the plates together, which would be halted by a signal from an acoustic detector when fracture occurs. It is instructive to record the fracture using high speed photography techniques. This allows the origin and nature of the fracture to be determined. The plate distance can be measured from the recording. The high speed camera used for recording is detailed in section 3.4.5. The camera captures the fracture from a side profile. The plate movement was controlled by a hand cranked drive screw (Figure 3.17).

![Image](image.png)

**Figure 3.17:** Illustration of two point bend test apparatus. The side profile of the glass is captured by a high speed camera allowing the plate distance and plate contact angle to be measured.

For large sample or especially flexible samples the contact angle $\theta$ is zero. In this case the Cosine term in (50) vanishes. Tests were performed on ultrathin glass and so $D \gg t$. Consequently $(D-t)$ in (50) can be approximated as $D$. The stress either side of the midpoint scales with $\sqrt{\sin \Psi}$, where $\Psi$ is the angle between the horizontal and the tangent to the bend. $\Psi$ varies between $0^\circ$ and $180^\circ$ from the midpoint of the sample to the end. The stress variation from sample midpoint to end is plotted in Figure 3.18.
Figure 3.18: Plot of the variation of bend stress in a substrate from the midpoint to the edge for a 130μm thick substrate. Bend stress is normalised to $\sigma_{\text{max}}$. The horizontal line represents the 80% stress threshold.

The two point bend test has numerous advantages over other bend test setups such as three or four point bend test. One significant advantage is that over half of the substrate experiences at least 80% of $\sigma_{\text{max}}$ which can be seen in the plot Figure 3.18. This is especially important for brittle materials such as glass as fracture is initiated at defects in the substrate. These defects occur stochastically in the material giving a statistical scatter in the results. By applying tensile stress to the glass uniformly the scatter can be reduced. There is no contact between the substrate under testing and the apparatus except along the short edge of the glass. This is acceptable as this edge does not experience any stress during testing. The contactless nature of the test prevents any contamination of the sample during testing. The apparatus is simple, requiring only a one axis movement rail and simple fixturing to perform tests. Samples of any size can be tested with minimal reconfiguration of the apparatus.

### 3.4.5 High Speed Photography

High speed photographic techniques were used to capture images of glass fracture. The camera used was a Phantom v310. This camera is capable of recording a frame rate of 3.25kHz at a resolution of 1280x800. Increasing the frame rate decreases the image resolution and makes sample illumination more demanding. The frame rate can be increased up 0.5MHz but with a significant reduction in image resolution to 128x8. Images are saved onto the internal volatile
camera memory during recording, as it is not possible to save images onto flash memory as the transfer rate is lower than the recording rate. The camera is mounted on an adjustable tripod with rotary screws allowing fine adjustment of the pitch, tilt and yaw. The camera is triggered by a low TTL signal. In the current setup the trigger was wired to a push button. While waiting for a trigger the camera is continuously recording and overwriting what is stored in memory. When the trigger is activated the camera will save a specified amount of images which occurred pre trigger and a certain amount post trigger. Depending on requirements the saved images can be entirely pre trigger, entirely post trigger or a mixture of both. After recording the saved video is transferred to a control PC for viewing and editing. The length of the recording is limited by the 8Gb of internal volatile memory.

A Nikon micro-NIKKOR zoom lens was used to magnify and focus the area of interest. The lens had a focal length of 105mm. Illumination was provided by two COOLH dedocool tungsten light heads. Each light used a 24V 250W halogen lightbulb. The housing contained an adjustable lens to allow focusing to maximise light intensity on the area of interest. Active cooling of the bulb was provided by an internal fan. For prolonged exposure some radiative heating of the work piece occurs. A COOLT3 control unit was used to power the light. The applied voltage could be varied from 21V to 26V depending on lighting requirements. The lights were setup to illuminate the sample stereoscopically (Figure 3.19).

Figure 3.19: Photograph of high speed imaging setup showing Phantom high speed camera, dual dedocool lights and COOLT3 control unit.
3.5 Computational Modelling

This section will outline software packages and computational techniques used to design experiments and interpret results.

3.5.1 Optical Design

Optical design was carried out using Zemax 12 engineering edition software (S/N 33397). Zemax is one of the industry standards for optical design and simulation. By defining a base optical system and a performance target Zemax will run algorithms to optimise the system. Zemax can also be used to non-sequentially trace rays through a system to examine scattering. Similar to the finite element method, the availability of high power low cost computers has seen optical modelling come into widespread use.

When designing and optimising optical systems the sequential ray tracing mode is used. Here rays start at the object surface propagate to surface 1, then surface 2 and so on in a predefined order until the final image surface is reached. Users define an optical setup which can include mirrors, lenses, waveplates or gratings. Generally optical components are loaded in from manufacturer catalogues. Each element has a particular glass type assigned to it, again catalogues from glass suppliers are available. The light entering this system is then defined, the important characteristics are the entrance aperture size, wavelength and intensity distribution. For all models in this work the aperture size is set as the size of the laser beam, the wavelength is set to the particular laser wavelength and the intensity distribution is Gaussian.

The program can then optimise the design of the system to meet a certain performance target. For example the optimisation procedure can be used to find designs that give the smallest focused spot possible, a spot with certain dimensions or certain wavefront curvature. When defining the parameters of each component of the optical system a label of either fixed or variable is applied. When running the optimisation parameters labelled as variables are altered to meet the performance target. Any attribute labelled as fixed is not altered. Variables can be set to have a maximum or minimum value which they cannot exceed. Prior to running the optimisation Zemax calculates the merit function \((MF)\) of the system using the expression (51). The merit function is a numerical representation of how closely the current system meets the performance target. The number is calculated from a list of operands which each determine
specific attributes about the current design \((V)\) and by how much it differs from the performance target \((T)\). Each operand has a weighting \((W)\) depending on its importance to the performance goal.

\[
MF^2 = \frac{\sum W_i (V_i - T_i)^2}{\sum W_i}
\]

(51)

When the optimisation is run, Zemax will begin altering the design of the system to find a minimum value of the merit function, subject to the boundary constraints. The optimiser is balancing achieving performance targets while also minimising aberrations in the system. Once the optimiser has arrived at a minimum value the optimisation procedure will stop. The optimised system may contain undesirable elements such as highly curved, very thick lenses or an unfeasibly large separation between lenses. It may be necessary to adapt the boundary constraints and repeat the optimisation to avoid such issues. The design entered may also not be suitable for the particular performance targets at all and additional lenses may be required. The optimiser will optimise surfaces already in the system but will not add or remove surfaces to improve performance. This must be done manually. Typically several optimisation cycles are required to arrive at a reasonable optical design. The beam size, polarisation, wavefront and encircled energy can be measured at any surface in the beam path.

Figure 3.20: A simple optical system designed in sequential mode. The system contains two elements, a plano-convex singlet lens and a flat mirror. The chief and marginal rays are drawn.
Zemax can also be used to carry out nonsequential ray tracing. Here we can define multiple light sources from which a prescribed number of rays propagate until they arrive at an object where reflection and transmission components will be calculated dynamically. At each surface the ray will be split into the transmitted and reflected rays which will then continue propagating. This exponential increase in the number of rays makes it computationally demanding. Stray light and scattering effects are accounted for in nonsequential ray tracing. Optical components and sources are designed in a similar fashion as the sequential ray tracing method. In this mode detectors can be placed at any point in the optical system to measure the beam characteristics. Optical systems tested in this mode will give a more realistic indication of performance.

Surfaces measured by AFM or surface profiler techniques can be imported into Zemax for analysis. It is also possible to generate surfaces using geometric shapes and Boolean operators for combination and subtraction of shapes. The nonsequential mode is useful for observing scattering, transmission and reflection off such surfaces.

### 3.5.2 Finite Element Method

The finite element method is a numerical method for solving partial differential equations which would be difficult, if not impossible, to solve analytically. The problem is discretised and appropriate boundary conditions are set. Linear equations are then applied to each part and the individual solutions are combined to reach the final approximate solution to the problem. The error in the solution is related to the number of discretised parts, similar to approximating a circle with a series of straight lines. Hrennikoff [138] and Courant [139] published early work on approximating a solution for partial differential equations in structural mechanics problems leading to the development of the finite element method. The decreasing cost of high power computers has seen this method come into widespread use in recent decades.

COMSOL multiphysics was used to perform finite element analysis (licence: 1044303). COMSOL provides an extensive library of physics modules to study various physical phenomena and allows coupling of solutions between modules. The thermal stress and structural mechanics modules were used in this work. A typical work flow for setting up a model begins with defining the dimensionality and geometry of the problem. Two dimensional models are preferred when a 2D ‘slice’ of the material is sufficient to achieve the desired
solutions and accuracy. Three dimensional models are more computationally intensive to solve. For example a simple heat conduction problem for a 2D square with sides of 1m involves solving for 578 elements and takes approximately 3s (dependent on mesh size). For a 3D cube with sides of 1m with identical parameters the same calculation involves solving for 16180 elements and takes approximately 24s. Domain geometries are then defined. Geometric shapes are available in COMSOL and, along with Boolean operators, allow any configuration to be defined. COMSOL also allows CAD files to be imported as a model geometry. A material type is then added to the domain. COMSOL contains an extensive material library with several material suppliers’ catalogues already defined. A custom material type can also be defined. Depending on the type of study only certain material parameters are required. For example to solve a linear elastic solid mechanics model the Young’s modulus, Poisson’s ratio and density are the only material parameters required. The particular physics module to be solved is then applied to the domain. Inside the physics module we also define boundary conditions and constraints. Considering a solid mechanics module again boundary conditions include fixed constraints, prescribed displacements and edge loads.

With the problem now fully defined, the last step is to discretise the domain. The default mesh divides the domain into triangular regions. The mesh size is user definable. The mesh is dynamic and can be concentrated around fine features in the domain to improve accuracy and prevent discontinuities. In larger, more uniform, regions the mesh will be coarser. Other mesh shapes and distributions are possible, however the triangular mesh was sufficient for this work. A solver for the model is then selected. For solid mechanics models the solution is generally invariant with time and a stationary solver is sufficient. For models using the thermal stress module a time dependent solver must be used as the solutions will vary with time due to thermal diffusion. An eigenfrequency solver computes the eigenmodes and eigenfrequencies of a linearised model. For the solid mechanics physics module this corresponds to the natural vibrational frequencies and mode shape of a body.
Figure 3.21: COMSOL simulation meshing and results. The left image shows a discretised 2D model of a plate containing an elliptical hole. Note the mesh concentration around the sharp ends of the ellipse and the coarseness in more uniform regions. The right image shows the solution, in this case the stress concentration the plate due to an applied tensile edge load, see section 2.5.1.

The structural mechanics module calculates stresses and strains in a body due to displacements or applied loads. A rigid body will experience stress due to applied loads or displacements which cause deformation. The relation between stress ($\sigma$) material displacement ($u$) and applied load ($F$) is given by (52). Loads can be applied to points, boundaries or the entire substrate.

$$\rho \frac{d^2u}{dt^2} = \nabla \cdot \sigma + F$$

(52)

The models used in this work assume the stress strain relationship is linear. For a linear stress strain relationship the expression (53) relates the two, where $\varepsilon_s$ is the material strain. The material parameters required for solving are the material density ($\rho$), Poisson’s ratio ($\nu_p$) and Young’s modulus ($E$). The material expansion in the directions perpendicular to the applied force is determined by Poisson’s ratio.

$$\varepsilon_s = \frac{\sigma}{E}$$

(53)

The thermal stress module is essentially the heat conduction in solids module coupled with the solid mechanics module. Temperature distributions and thermal expansion are calculated initially by the heat conduction module. Thermal expansion leads to displacement
fields in the material which are used as inputs for the solid mechanics module to calculate stress and strain values. The heat conduction in solids module calculates heating and cooling rates in a substrate due to conduction, convection and radiation. For solid materials over short time durations heat conduction is generally the dominant mechanism. Conduction is driven by temperature gradients in the material. The diffusion of heat in a substrate due to conduction can be calculated using the heat equation (54).

\[
\frac{\partial T}{\partial t} c_p \rho = k_T \nabla^2 T + Q(r, t)
\]  \hspace{1cm} (54)

This module takes the material density (\(\rho\)), material temperature (\(T\)), thermal conductivity (\(k\)) and specific heat capacity (\(c_p\)) as inputs. The heat source (\(Q\)) is defined by the user; for laser heating models the source has a Gaussian spatial distribution and pulses periodically over time. Typically \(k\) and \(c_p\) have a temperature dependence and are recalculated depending on \(T\) at each solver iteration.

### 3.6 Summary

This chapter describes the operation and basic theory of the tools used to perform experiments and analyse results. The manufacture and properties of glass samples used in scribing experiments and the laser systems used to mark the glass samples were described. The techniques applied during sample scribing, post processing and data analysis were then outlined. Microscopes and other characterisation tools are then described. Finally the computational software packages used in simulations were defined.
Lasers are versatile tools for material processing. This chapter examines the cut quality and processing speed of scribes and cuts made with various laser sources. Each laser source has unique properties with inherent advantages and disadvantages. The purpose is to review and benchmark glass processing with conventional laser techniques.

4.1 Introduction

Cutting is the most common use of a laser; 80% of industrial lasers in Japan are used for cutting [57]. Lasers offer numerous advantages over traditional mechanical cutting methods. Laser processing is non-contact, eliminating tool wear and allowing sterile devices to be produced. Processing speeds are generally higher than mechanical cutting with a narrow kerf width. Laser processes lend themselves to easy automation and reconfiguration.

The laser sources used in the tests are a long pulse CO₂ laser, a short pulse UV laser and an ultrashort pulse IR laser. Due to contrasting photon energies and pulse durations each laser has fundamentally different absorption and thermalisation mechanisms producing diverse processing results. Laser material removal mechanisms can be thermal, photophysical or photochemical. For long pulse durations and strong absorption the material removal takes place through thermal melting and boiling. As the pulse duration is decreased material removal becomes more complex with photochemical and photomechanical effects becoming significant. For ultrashort pulse durations nonlinear effects such as material desorption, multiphoton ionisation and avalanche breakdown are dominant.

The inefficiency of the laser material removal process can be understood with a simplistic energy balance model. Consider the energy required to melt and completely vaporise a 10μm diameter and 10μm deep cylindrical crater in a silica substrate. The volume to be removed is 7.85x10⁻¹⁶m³ corresponding to a mass of 1x10⁻⁹g. An idealised heating and boiling
model indicates that an energy of 14.1µJ is required to boil and vaporise this material. Experimentally a laser pulse incident at this energy will, depending on the parameters, have no visible effect on the surface or will cause a small increase in temperature. In reality we have surface reflection, partial absorption by the glass and subsequent plasma plume absorption, during ablation and vaporisation, which reduce the applied energy transferred to the material. The energy requirement will be increased by effects such as thermal conduction during the laser pulse and surface emissivity. However the energy requirement will also be reduced by liquid material expulsion from the cut and material fracture and ejection. The analysis becomes complex when all of the variables are considered. It is clear the optical energy in the laser pulse is not efficiently used in typical material removal process.

Ideally a piece of glass cut by a laser would have an optically smooth cut face (Ra≤100nm), no chipping or cracks along the cut edge and a post processing fracture strength of >200MPa. Low surface roughness is beneficial for applications such as LED devices to maximise the amount of outputted light by reducing scattering. Chipping or cracking will reduce the strength of the cut piece, a stress of 200MPa is a typical stress an LED device or PV device will experience if heated and cooled rapidly. The fracture strength can be measured using the two point bend test method (section 3.4.4) and compared by fitting the acquired data to a Weibull cumulative distribution (section 3.3.7). Cut face roughness can be quantified using optical surface profiling techniques (section 3.4.2). Chipping and cracking can be observed using optical microscopy techniques (section 3.4.1). The process must be completely reproducible and the overall scribing speed must be >100mm/s for the process to be economical and disruptive to current glass cutting techniques. The objective of this chapter is to quantify the previously mentioned parameters for various laser cutting process and compare the results. Parametric studies will be carried out to optimise performance.

### 4.2 CO₂ Laser Glass Processing

CO₂ lasers are, at first glance, ideal candidates for glass processing. A mature and economical technology which emits light at wavelengths which are strongly absorbed by glass substrates (10.6µm). The absorption coefficient for silica at this wavelength is estimated at 250cm⁻¹ [42]. The photon energy of a CO₂ laser (0.12eV) is in resonance with the excitation energy of the first vibrational level in a silica molecule, typically between 0.01eV and 0.1eV [42]. Absorption takes place through resonance absorption in SiO bonds. The refractive index of glass is also
high at this wavelength giving a reflectivity of 20% for fused silica. CO₂ lasers are generally available in long pulse or continuous wave output modes resulting in significant thermal diffusion and therefore large heat affected zones (HAZ).

A full body laser cut can be achieved using a focused CO₂ laser to vaporise a trench through the entire substrate. The laser energy is set at a high enough level to cause significant heating and boiling of the substrate. Material removal in this case takes place primarily through boiling and vaporisation [42, 57]. CO₂ lasers typically do not reach an intensity sufficient to cause significant ionisation of the vaporised material leaving the surface [42]. The vapour leaving the surface will cause attenuation of the incident laser due to absorption and scattering. There will also be some distortion of the laser spot shape. The absorption of the laser changes dynamically over the course of the removal process. A CO₂ laser incident on a glass substrate first heats up the surface to vaporisation point creating a ‘keyhole’ recess. Keyhole formation marks an increase of absorption, as the considerable laser energy which was being reflected away from the surface undergoes multiple reflections in the keyhole. Process efficiency is improved.

To estimate the material removal rate we can again consider the energy balance approach discussed briefly in the introduction (section 4.1). With the assumption that material removal takes place only through vaporisation we can estimate how much vaporisation will take place for a given amount of energy incident on the substrate. Energy is consumed in melting and vaporisation processes. The depth reached $\Delta h$ during a laser dwell time $\tau_d$ is given by (55). For most materials the change in enthalpy is $(\Delta H_v, >> \Delta H_m + \rho c_p \Delta T)$ and the right hand approximation in (55) holds [42].

$$\Delta h \approx \frac{\tau_d (AP - P_L)}{F[\rho c_p(T - T_0) + \Delta H_m + \Delta H_v]} \approx \frac{A \phi - \phi_L}{\Delta H_v} \quad (55)$$

$A$ is the dimensionless absorptivity of the material at the relevant wavelength and is assumed constant. $P$ is the average laser power. $P_L$ accounts for energy radiated from the surface, thermal conduction in the material and energy remaining in material which is not vaporised. $P_L$ is therefore material dependent. $F$ is the area removed. $T$ is the average temperature at which vaporisation takes place. The specific heat capacity $c_p$ is assumed to be constant for all phases of the material. $\Delta H_m$ and $\Delta H_v$ are the enthalpies of melting and vaporisation respectively. $\phi$ is the applied fluence and $\phi_L$ is energy not used in material removal processes. Attenuation of the laser due to the vapour plume is ignored. Recondensation of the material within the process area along with material ejection is assumed to be zero. The right
hand approximation of expression (55) is plotted in Figure 4.1. For thermal ablation $\varphi_L$ remains constant when $\tau_L$ is fixed [42]. It is clear from Figure 4.1 that efficiency can be increased by reducing the $\varphi_L$ term, hence minimising collateral heating of the substrate. This is best achieved by reducing the laser pulse duration and thus reducing the time in which thermal conduction can occur. The heat diffusion length ($l_T$) is given by the expression [42] $l_T \approx 2\sqrt{D\tau_L}$. $D$ is the thermal diffusivity of the material and $\tau_L$ is the pulse duration.

![Thermal Ablation Depth vs. Applied Fluence](image)

**Figure 4.1:** Plot of expression (55) for typical CO$_2$ laser processing parameters. Absorption is assumed to be unity, $\Delta H_v=1.26 \times 10^7$ J/kg.

There are two distinct regimes of material evaporation which can occur depending on laser fluence. For intensities on the order of GW/cm$^2$ and long laser pulses, surface evaporation dominates [42]. For high fluences phase explosion becomes significant [49]; the material becomes overheated to a critical temperature and explosive boiling takes place. This transition coincides with an increase in material removal rates. Vaporised material leaving the surface will exert a pressure on the surface due to conservation of momentum. This may assist in material removal by breaking off material fragments or pushing molten material out of the kerf. The recoil pressure can be estimated using $P_{rec}=10^{-5} I_{abs}$. For metal cutting Gagliano [140] estimated that 60% of the material removed was due to material ejection. By applying a coaxial air nozzle to the laser beam output it is possible to shear molten material along the kerf and out the rear surface of the cut. In this case the heat of vaporisation of the material need no longer be surpassed resulting in an increase in efficiency of approximately 90% [57].
As an alternative to a vaporisation process, a CO$_2$ laser can be used to achieve controlled fracture of glass [55]. The edge of the glass is scribed with an edge notch using a diamond scribe. The laser is used to heat the material to a temperature below its melting point. Subsequent to laser heating a coolant air jet is applied to heated region. Rapid cooling causes the stress to become tensile and cause the pre-existing crack to extend. The tensile stress peaks in the centre of the laser spot ensuring the crack extension is controllable. This method is widely used in industry for processing glass of half a millimetre to several millimetres thickness. Processing speeds of 300mm/s are reported for 1mm thick soda lime. Thermal fracture is applied to thin glass cutting in the next section.

### 4.2.1 Experimental Method

The laser used for glass processing was a Coherent diamond Gem-60 CO$_2$ laser. The laser configuration is outlined in section 3.2.3. The laser was incident on the sample from above (Figure 4.2). The sample was positioned in the laser focus using a CNC Z stage. The laser was scanned across the sample by moving the stage relative to the stationary laser. The glass material used was Corning borosilicate ‘Willow’ glass, which had a thickness of 130µm. A coaxial air nozzle delivered air to the laser interaction zone at a pressure of 20kPa. This prevented contamination of the objective lens during sample processing. Laser power was measured with a power meter (Thorlabs). The power was varied by adjusting the pulse duration of the signal generator triggering the laser. When necessary the sample was cooled by a cool air jet emitted from a compressed air vortex cooler (Meech). The cooler emitted an air jet with a temperature of approximately -5°C.
The objective lens was a 38mm focal length ZnSe meniscus lens. The optical setup gave a focused spot diameter \((1/e^2)\) of 162\(\mu\)m. The laser was defocused by \(\sim\)10mm to increase the kerf width. This prevents molten glass beading and forming a bridge across the cut. This bridge solidifies as the glass cools preventing effective separation of the substrate. The defocused spot size was 264\(\mu\)m calculated using equation (46). The laser settings used for glass cutting were 10kHz rep rate, 30W average power, 3000\(\mu\)J pulse energy, 40\(\mu\)s pulse duration and 70mm/s scan speed. These settings were chosen to maximise the cut speed and minimise stray fracture. The applied fluence was 10.9Jcm\(^{-2}\). The laser spot overlap was 97.35\%. One laser pass was sufficient to achieve a complete cut through the substrate.

Sample characterisation was carried out using SEM, optical microscopy and white light interferometry techniques (see section 3.4). To characterise the scribe profile the cross sectioning technique described in section 3.3.4 was used. The processed sample strength was determined using the two point bend test method (section 3.4.4).

### 4.2.2 CO2 Laser processing results

Figure 4.3 shows CO\(_2\) laser full body cuts made in glass using the laser parameters indicated in section 4.2.1. The high absorption coefficient results in the laser being heavily absorbed in a thin surface layer causing rapid heating. The long pulse duration allows time for significant
thermal diffusion to occur during the laser pulse. For a 40µs pulse we have estimated a heat diffusion length of 11.9µm using the expression \( l_T \approx 2\sqrt{D\tau} \). This results in a large heat affected zone, an edge burr and in most cases catastrophic, uncontrollable fracture of the glass. Fracture usually occurs near the edge of the laser interaction zone and is caused by tensile stress induced during conductive cooling. Fracture can occur as much as several seconds after the laser interaction. The substrate was completely cut by the laser vaporisation process and no mechanical force was required to separate the pieces. Some bending of processed samples was observed.

Figure 4.3: SEM image of thin glass substrates cut by thermal ablation using a CO\(_2\) laser. The left image shows a full body cut edge with the sample tilted by 45° towards the detector. The right image shows a cross section of a full body cut. Significant edge burr is visible in both images.

The roughness of the cut edge was measured using an optical surface profiler. The processed sample was mounted on an angled stub with a carbon tab. The sample was placed in the focus of the objective lens of the surface profiler. Results indicate a smooth cut face with an Ra value of 260±13nm (Figure 4.4). The cut face is not orthogonal to the sample surface, a hump of approximately 6.5µm was measured with the surface profiler.
Figure 4.4: Surface profiler measurements of cut edge roughness for a glass substrate cut by thermal ablation using a CO$_2$ laser. The top image shows a 2D map of the cut edge with the colour scale indicating height. The lower image shows line plots taken at various points across the sample surface.

Rectangular 50mmx10mm samples for a two point bend test were produced. Samples were warped by several millimetres due to the laser interaction. Ten samples were tested and the data was fitted to a Weibull cumulative distribution. Figure 4.5 shows the results of the analysis. The 10% failure threshold occurs at 155±9MPa.
Figure 4.5: Results of two point bend test on CO\textsubscript{2} laser processed willow glass samples. The dashed plot shows the Weibull cumulative distribution with parameters fitted to the measured data. Data points are indicated on the plot. The inserted image shows a sample under inspection in the two point bend test. The image shows the sample immediately prior to fracture. $\sigma_{\text{max}}$ at fracture is 252MPa.

Controlled fracture of the glass was carried out using a lower laser power and scribing the edge of the glass with an edge notch using a diamond scribe (Figure 4.6). The laser power was lowered to 10W, sufficient to heat but not melt or vaporise the substrate. A coolant jet was applied immediately behind the laser spot. The exact lag distance was difficult to determine accurately as the coolant jet spread out after leaving the nozzle. The edge was scribed with a 3mm scribe using a diamond tipped scribing tool. The scan speed was reduced to 20mm/s. The laser started off at the edge of the sample and was scanned across. The crack could be seen propagating behind the laser spot almost instantaneously. The fracture produced was nearly through the glass, only a small amount of mechanical force was required to separate the pieces. Occasionally the fracture strayed from the straight line defined by the laser, especially as the crack approached the edge. The process was unreliable, and it was not possible to produce accurate samples for a two point bend test.

Figure 4.6: SEM images of the cut edge of thin glass samples fractured using laser induced fracture technique. The samples are tilted by 45° away from the detector. The left image shows the top surface and right image the bottom surface. Faint Wallner lines are visible.

As the surface was formed by brittle fracture as opposed to a boiling and vaporisation process, it has low surface roughness (Ra=79±3.9nm). The cut face is orthogonal to the surface (Figure 4.7).
4.2.3 Thermal FEM Analysis

A two dimensional FEM model was developed in order to more precisely quantify the role of pulse duration and duty cycle in the material vaporisation process. The model used the heat conduction in solids physics module. A 0.13mmx1mm rectangle was defined, representing a cross section of a willow glass substrate. To mimic the effect of laser heating, a heat source with a Gaussian distribution across the beam spot and an exponential decay with increasing laser path length was defined. The rate of decay is proportional to the absorption coefficient of 10.6μm wavelength light in a glass substrate ($\alpha=250\text{cm}^{-1}\text{for SiO}_2$\cite{42}) according to the Beer-Lambert law. The laser pulse width is represented by a pulse with the appropriate temporal characteristics. The built in rectangle function was used to switch the heat source on and off over time. The rectangle function was smoothed to prevent discontinuity errors. Discontinuity errors can arise when a coefficient or material property contains a step function, and can lead to convergence errors in the solver. The power density of the heat source is related to the laser pulse energy by dividing the peak power of the laser by the interaction volume. The interaction volume is taken as the cylindrical volume defined by the spot radius (162μm) and optical
penetration depth \((1/\alpha=40\mu\text{m})\). Material properties for borosilicate glass were loaded from the material library. Material boundaries are assumed to be insulating. The model dimensions were sufficiently large that the regions close to the vertical edge boundaries were negligibly heated and edge effects were not important. Emissivity from the surface was initially considered, however the effect is negligible for such a small area, relative to the thermal diffusivity. A uniform, free triangular mesh was applied to the substrate. Mesh size was set to ‘extremely fine’ which plotted 3280 domain elements into the geometry.

Figure 4.8 shows the result of the FEM laser heating model. Three simulations were designed, two at a 10kHz repetition rate with a 40\(\mu\text{s}\) and 10\(\mu\text{s}\) laser pulse, and one at a 100kHz repetition rate with a 10\(\mu\text{s}\) pulse. The 10kHz and 100kHz repetition rates give a pulse period of 100\(\mu\text{s}\) and 10\(\mu\text{s}\) respectively. A time dependent solver was used which found numerical solutions to the heat equation at prescribed time intervals. Initially the substrate was set at a uniform temperature of 293K. The heat source was switched on for the prescribed time. For the 40\(\mu\text{s}\) pulse duration ten solver time steps of 10\(\mu\text{s}\) from 0 to 100\(\mu\text{s}\) were used. For the ns pulse a 2\(\mu\text{s}\) solver time step was required to solve for the pulse. A large time step was used after the pulse had switched off to solve to the end of the pulse period, a 1\(\mu\text{s}\) step for 100kHz and a 10\(\mu\text{s}\) step for 10kHz.

Solving for multiple pulses in a single simulation was not feasible due to significant computational memory requirements. To bypass this issue an individual simulation for each pulse was carried out. The temperature distribution was saved and the memory cleared. The saved temperature distribution was set as the initial conditions for the next pulse. The simulation was run again to solve for the temperature distribution after two pulses. This procedure was manually repeated to solve for \(n\) pulses. Additional loops were run until the peak temperature in the material had reached the vaporisation temperature of borosilicate glass (~2500K). This is the temperature at which material removal will begin. For short laser pulses, the temperature at which material removal takes place will exceed this value due to overheating.
Figure 4.8: Results of FEM simulation of laser heating in a 2D glass material. Image (a) shows a 2D surface plot of the temperature distribution in the glass substrate after the simulated laser interaction. The results of three simulations are plotted, the specific laser settings are indicated on the plot. The colour scale indicates temperature. Image (b) shows a line plot along the top surface of the glass substrates. The spot diameter of the laser and the melting temperature of borosilicate glass are indicated on the plot.
4.2.4 Discussion

CO₂ lasers are capable of producing full body cuts in glass. Reasonable speeds can be achieved (70mm/s) by employing a vaporisation process and high quality cuts can be achieved by employing a controlled fracture process. However the process is unpredictable due to thermal stress induced by the rapid heating coupled with the brittle nature of thin glass.

Full body cuts (Figure 4.3) show a smooth cut face but a significant burr with a height of 150µm from the glass surface. The processing speed is 70mm/s which is comparable to mechanical glass cutting techniques. There is a significant heat diffusion length due to the long pulse duration (11.9µm). For the vaporisation process, the material to either side of the laser interaction zone is heated to above the melting temperature. Once the material is molten the surface tension deforms the liquid into a droplet shape. The material then cools and solidifies in this shape. This is the cause of the large edge burr seen in Figure 4.3. The coaxial air jet may also be contributing to the elongation of the molten glass burr from the rear surface. Processing of heat sensitive devices such as organic LEDs is not feasible due to the significant collateral heating. The rapid heating of the substrate leads to rapid cooling, driven by the steep temperature gradients. Tensile stresses will occur in the cooling regions. Tensile stresses are more likely to cause fracture in the material as they are amplified by material flaws (see section 2.5.1). Consequently spontaneous uncontrollable fracture is observed in a significant number of samples. The fracture typically occurs around the edge of the laser interaction zone, where tensile stresses are highest. Fracture is sometimes delayed by several seconds after the end of the laser pulse. Surface roughness was measured using a white light interferometer and has an Ra value of 260±13nm. The molten edge layer will reflow due to surface tension and ‘fill in’ any irregular features on the surface. This is similar to the fire polishing technique used in glass manufacture. The fracture strength after processing is poorer than the desired 200MPa 10% failure threshold goal. The warping of the sample produced for the bend test is likely due to residual stresses remaining in the processed glass after cooling.

Laser fracture (Figure 4.6) produced excellent quality cuts with a processing speed of 20mm/s which is close to the desired range. Scribing of the edge notch with a diamond scribe caused undesirable microcracks. As the crack approached the edge of the sample the stress fields become more complex and the path tended to deviate from the path defined by the laser. Consequently it was not possible to produce an accurate sample for a two point bend test. The surface roughness is low, Ra=5nm, as expected from a fracture surface (Figure 4.7). The cut
face is highly orthogonal to the sample surface. The fracture process shows promise and delivers excellent quality cuts but lacks precision when applied in this form.

The FEM analysis shows the effect of pulse duration and duty cycle on the heat affected zone clearly. For a long pulse duration laser a significant amount of material outside the laser spot is heated. Some of the material is heated to above the melting temperature, but below the vaporisation temperature, which will lead to an edge burr as seen in Figure 4.3. Shortening the pulse duration to 10ns reduces the heat affected zone. Increasing the duty cycle, by increasing the repetition rate, leads to further reductions in the heat affected zone. Based on this analysis optimal thermal ablation conditions require a short pulse duration and high repetition rate. When the pulse duration is too short the laser will heat the surface to a temperature much greater than the vaporisation temperature. Overheating of the evaporated material will reduce the ablation efficiency.

### 4.3 Nanosecond UV Laser Glass Processing

Repetitively pulsed nanosecond lasers offer a precise and relatively low cost method for material processing. Depending on material parameters collateral damage around the laser interaction zone can be negligible. This occurs when the material removed per pulse is close to the heat penetration depth \( l_T \approx 2\sqrt{D\tau_l} \) or optical penetration depth \( \alpha^{-1} \), whichever is larger. This condition can be satisfied for many materials with a UV wavelength nanosecond pulse length laser due to the higher absorption coefficient of UV wavelengths. Metals do not meet this condition for nanosecond pulses due to large values for thermal diffusivity. Precise processing of glass is also difficult due to the negligible linear absorption of UV, VIS and NIR wavelengths \( \alpha << 1 \text{cm}^{-1} \). The primary application of short pulse lasers is surface patterning and processing of materials which are problematic to process by other techniques\[141, 142\].

IR laser wavelengths will linearly excite conduction band electrons when processing metals. Glass is an insulator with an empty conduction band and a typically large material bandgap. For interband absorption to occur in glass a wavelength of approximately 310nm would be required to excite an electron across the bandgap. Endert et al \[143\] report on silica patterning using a 157nm excimer laser. At longer wavelengths large bandgap materials, such as glass, absorb energy mainly through bulk defects, surface states and partly-free seed electrons \[42\]. UV lasers are more suitable than longer wavelengths for short pulse laser glass
processing, due to the higher photon energy increasing the probability of absorption in material defects. Defects are also generated by repeated laser irradiation. Laser induced defects are referred to as incubation centres. These can include colour centres, vacancies, broken bonds and molecular fragments [42]. An effective absorption coefficient to account for these effects can be expressed as (56).

\[
\alpha = \alpha_0 + \sigma_i N_i + \alpha_D N_l + \alpha^{NL}
\]  

\(\alpha_0\) is the linear absorption coefficient, \(\sigma_i\) and \(N_i\) are the excitation cross section and density of material defects. \(\alpha_D\) accounts for laser induced defects and is saturated after \(N_l\) pulses. \(\alpha^{NL}\) accounts for non-linear absorption processes. It is clear from (56) that there will be some spatial dependence in \(\alpha\) as \(N_i\) is irregular throughout the material.

Ablation mechanisms for short laser pulses encompass a combination of thermal, mechanical, photophysical, photochemical and defect models [42]. The dominant mechanism is dependent on material properties and laser parameters. Coupling of laser energy into the substrate will take place through single or multiphoton processes, depending on the band structure. Defect state excitation will also occur depending on the defect concentrations in the material. Thermal ablation occurs when rapid thermalisation of this energy leads to vaporisation of the material volume or high stresses leading to material fragmentation. With sufficient photon energy chemical bonds in the material can be broken and material will desorb from the surface in a photochemical ablation mechanism. Pure photochemical ablation will occur with no change in material temperature. Material desorption can also lead to stress build up and fragmentation in the material. Photophysical ablation refers to a combination of thermal and non-thermal ablation mechanisms.

Other less dominant absorption pathways include multiphoton ionisation and avalanche ionisation. During multiphoton ionisation two or more photons are absorbed simultaneously and the sum of their energies is sufficient to promote an electron from a bonding to a non-bonding state. The free electrons generated are highly absorbing of further photons through inverse bremsstrahlung. Excited free electrons can ionise additional electrons in a positive feedback process known as avalanche ionisation. Scribing of high aspect ratio features is problematic for nanosecond scale pulses due to attenuation of the incident laser by ablated material confined within the trench.

Nanosecond lasers can reach intensities sufficient to ionise material leaving the material surface. The pulse duration is not short enough to avoid some of the pulse interacting with the
plasma plume [144]. The plasma plume will attenuate the incident laser negatively affecting process efficiency. The expansion rate of the plasma plume is tied to the laser spot size. Typically a smaller spot size will give higher ablation rates until a certain saturation value is reached [145]. A smaller spot will result in a smaller plasma plume which will diffuse at a higher rate than a larger plume, resulting in less attenuation of the incident beam. Material removal mechanisms tend to be non-equilibrium.

### 4.3.1 Experimental Method

The laser used was a Spectra Physics high peak power oscillator (HIPPO) laser (see section 3.2.2). The HIPPO laser emits a 1064nm wavelength beam with a pulse duration of 15ns. A third harmonic generation head was attached to convert this to a 355nm output with a 12ns pulse duration. The laser was incident on the sample from above (Figure 4.9). The sample was focused on the sample surface using an F theta lens. The glass material used was Corning borosilicate ‘Willow’ glass which had a thickness of 130µm. The laser was operated at full power, giving an average power of 5.5W at a repetition rate of 30kHz. The corresponding pulse energy is 183µJ. Spot sizes were calculated by ablating a series of craters with varying pulse energies and plotting of the square of measured crater diameters against the natural log of the pulse energy [133]. The error in the spot size was taken as the error in the least squares linear fit function. The focused spot diameter (1/e²) was 16.4±0.8µm giving an applied fluence of 173±8.65J/cm². The galvo scanner system was used to scan the beam at a speed of 400mm/s. This gives an overlap of 18.7% (SPA=1.23) between successive laser pulses.
Sample characterisation was carried out using SEM, optical microscopy and white light interferometry techniques (see section 3.4). To characterise the scribe profile the cross sectioning technique described in section 3.3.4 was used. The processed sample strength was determined using the two point bend test method (section 3.4.4).

### 4.3.2 NS UV Processing results

Figure 4.10 shows a process window for UV short pulse laser ablation of glass in terms of the applied fluence and spot overlap. The samples were scribed using the laser configuration outlined in Figure 4.9. Scribes were made across a range of applied fluences and spot overlap values by changing the pulse energy and galvo scan speed. 30 laser passes were used in each scribe. Any scribe which showed microcracking, or chipping >20μm was deemed unacceptable. The maximum laser fluence within the acceptable process window (173J/cm²) was used for glass scribing experiments. This gives the maximum processing speed. To achieve microcrack free scribes a low overlap was used (SPA=1.23).
Figure 4.10: Pictorial graph showing the process window in borosilicate glass for UV NS laser ablation. A green outline indicates acceptable scribe quality, a red outline indicates unacceptable quality. The onset of microcracking along the scribe defined the edge of the process window.

The stochastic nature of nanosecond laser ablation can be seen from the optical microscope image presented in Figure 4.11. After 20 laser passes parts of the sample are ablated nearly entirely through the substrate while an adjacent parts of the sample are visibly unaffected by the laser. Ablation occurs on the front and the rear surface of the glass. Chipping is visible along the kerf edge.
Figure 4.11: Microscope images of glass sample after irradiation with NS UV laser. After 20 passes ablation has occurred sporadically at the front surface, rear surface and in some parts not at all. 50 passes are required to achieve a consistent cut through the glass.

Figure 4.12 shows a cross section of a substrate scribed with 20 laser passes. The substrate is ablated from the front, rear surface and, in image (c), both surfaces. Kerf width and shape are non-uniform along the scribe. 50 passes are required for a consistent cut through the substrate.

Figure 4.12: SEM images of cross sectioned UV NS laser scribed samples. The laser was incident on the top surface in each image. Ablation can be seen occurring at the front surface (a), the rear surface (b) and both the front and the rear surface (c).

The edge quality of the cut glass is shown in Figure 4.13. The glass was scribed with 50 laser passes to achieve a consistent cut. The edge is free from micro cracks and is
reproducible but shows significant chipping and high roughness. No spontaneous stray fracture is occurring.

Figure 4.13: SEM image of a thin glass substrate cut by a UV NS laser. Sample is tilted 45° towards the detector. The left image shows the upper surface of the glass and the right image the lower surface.

The edge roughness was quantified using a surface profiler. The reflection from the surface was poor due to blackening of the surface and chipping. Consequently some areas of the surface could not be measured. A ~30nm thin gold coating was sputter coated to increase the reflected signal strength and improve the surface profile. The cut surface had a high roughness with an Ra value of 1.09±0.11μm.
Figure 4.14: Surface profiler measurements of cut edge roughness for a glass substrate cut by laser ablation using a nanosecond UV laser. The top image shows a 2D map of the cut edge with the colour scale indicating height. The lower image shows line plots across the sample surface.

50mmx10mm samples were produced for a two point bend test. 15 samples were produced. The top surface of the sample denotes the side which the laser is incident on. The bottom surface denotes the opposite side. Ten samples were tested with the top surface facing upwards in the two point bend test and five were tested with the bottom surface facing upwards. No noticeable difference in the magnitude of the results was found between the two tests. The statistical scatter is slightly reduced for the rear surface tests. The results were fitted with a Weibull cumulative distribution and plotted together in Figure 4.15. The 10% failure threshold occurred at 136±2.8MPa.
4.3.3 NS UV Laser Glass cut discussion

Nanosecond UV lasers show more precision and consistency for glass cutting compared with vaporisation processes but at a low overall processing speed (8mm/s). Heat diffusion scales with the square root of the laser pulse duration. For a 12ns pulse length we have a reduced heat diffusion length of 0.21µm. Consequently there is little collateral heating of the substrate and so we see no significant edge burr or micro cracking. The process is fully reproducible. Cut face quality is poor (Figure 4.13) with considerable chipping occurring. Chipping along the edge is not only an aesthetic issue it also detrimentally affects the glass strength. The results from the two point bend test show the glass is severely weakened with a 10% failure stress of 136±3MPa.

At low numbers of passes only parts of the sample which contain defects or contaminations will absorb the laser. Defects in the glass are randomly distributed and therefore the initial ablation is highly stochastic in nature. At high numbers of passes we begin to see incubation effects such as the formation of colour centres which enable coupling of laser energy into the substrate where it previously did not occur. This laser configuration is unsuitable for
scribe blind trenches, holes or other shallow features in a glass substrate, due to the unpredictable initiation of the ablation. It is not possible even to predict whether ablation will occur at the front, rear surface or occur at all as seen Figure 4.11 and Figure 4.12.

Figure 4.12 (c) appears to show ablation occurring at the front and rear of the glass substrate. Initially the laser passes through the defect free front surface of the glass. Once it reaches the rear surface defect states and impurities enable coupling of the laser energy into the substrate and we have ablation. After repeated laser passes we begin to see incubation effects on the front surface and which then cause absorption of the laser pulses leading to ablation at the front surface (Figure 4.16).

![Diagram](image)

Figure 4.16: Illustration of the potential effect of material defects and colour centres on short pulse laser ablation. Initially the laser is transmitted through the substrate and is absorbed by rear surface defects leading to material ablation. Repeated irradiation leads to the formation of colour centres at the front surface. Further laser pulses are absorbed at the front surface leading to ablation.

### 4.4 Femtosecond IR Laser Glass Processing

Ultrashort pulse lasers potentially offer a sustainable, reconfigurable and versatile solution for structuring thin glass. The key features of ultrashort lasers are their ability to reach the high intensities required for nonlinear absorption in glass at moderate pulse energies and highly localised energy deposition [26, 146, 147]. Due to the short interaction time thermal diffusion into the material is negligible. Ultrashort laser pulses allow damage free processing of metals and materials with high thermal diffusivity due to the insignificant thermal diffusion length. Kurt et al [148] illustrated this effect clearly by comparing feature quality in a steel substrate processed with 3.3ns and 200fs laser pulses. High thermal diffusivity in the nanosecond case results in an appreciable heat affected zone, while thermal affects are negligible in the ultrashort
case. Screening of the laser pulse by the ionised material plume is strongly reduced for picosecond pulses and negligible for femtosecond pulses.

For transparent materials the pertinent feature of ultrashort lasers is the high intensity, enabling nonlinear absorption mechanisms to take place. Laser absorption in the material is enhanced and precise processing is possible. Ultrashort lasers can manufacture a range of structures in glass, such as trenches, bevels, local surface or bulk changes in refractive index [149] and high aspect ratio drilled holes [150]. Sub-micron ablation precision is possible with femtosecond pulses [151] due to the absence of thermal effects and deterministic damage threshold. This laser, combined with a CNC scanning system allows complex features to be quickly and precisely machined on a dielectric surface or bulk substrate. Techniques for improving feature quality and processing speed are of interest especially for industrial applications.

Material removal mechanisms in the ultrashort regime include Coulomb explosion, phase explosion, spallation and fragmentation into the plasma state (see section 2.3.3). The dominant material removal mechanism is dependent on the laser parameters. Typically a nonlinear increase in ablation rate with fluence is observed [42].

4.4.1 Experimental Method
Scribing was performed using an Amplitude Systemes s-Pulse laser with a wavelength of 1030 nm and a pulse duration of 500 fs (see section 3.2.1). The laser emitted a linearly polarised beam which had a Gaussian beam profile with a nominal propagation factor $M^2<1.2$. The laser power was varied using the built in laser attenuator which consisted of a motorised half waveplate and a linear polariser. The glass used was 110 mm thick AF32 alkali free glass (Schott). A galvo scanner with a 100 mm focal length telecentric lens (NA=0.71) and a 20x microscope objective (NA=0.015) were used to focus the beam onto the sample depending on the desired spot size. Where necessary, a beam expander was used to expand the beam, and reduce the beam divergence angle, prior to entering the galvo scanner. Assuming the expander optics are diffraction limited this will give a smaller focused spot. The laser was incident on the sample from above. When focusing with the microscope objective the laser was scanned along the sample by moving the stage. During multipass scans the sample was moved towards the microscope objective by 1μm every ten passes to compensate for the small depth of focus.
of the microscope objective (316µm). This maintained the laser focus at the bottom of the scribe. A slotted stage was used to ensure the glass was open to air at the rear surface. Waveplates were arranged in the beam path before the objective lens to alter polarisation. A half waveplate was used to alternate between S and P polarised states and a quarter waveplate was used to convert from linear to circular polarisation. The polarisation state of the laser was determined using a Brewster window. HF etching was carried out as described in section 3.3.6.

Pulse energies and scan speeds were chosen so that the laser fluence and overlap matched across experiments (Table 4.1). A lower repetition rate was used for the microscope objective test as the scanning speed was limited by the stage movement speed. Laser power was measured with a power metre (Ophir). Spot sizes were calculated by ablating a series of craters with varying pulse energies and plotting of the square of measured crater diameters against the natural log of the pulse energy [133]. The error in the spot size was taken as the error in the least squares linear fit function. The single pulse applied damage threshold of the glass with this experimental setup was measured to be 4.37J/cm². Sample transmission was measured by a beam profiler (Ophir BeamstarFX33) placed beneath the sample. The laser energy was reduced below the saturation level of the profiler by fitting a 3.0 neutral density filter to the detector.

Table 4.1: Laser settings for ultrashort laser glass cutting experiments.
Objective Lens: | Galvo Lens | Galvo Lens | Microscope Lens |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Power:</td>
<td>1.74W</td>
<td>0.435W</td>
<td>50mW</td>
</tr>
<tr>
<td>Repetition Rate (kHz):</td>
<td>10</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Pulse Energy (μJ):</td>
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<td>43.5</td>
<td>10</td>
</tr>
<tr>
<td>Spot Diameter (1/e²) (μm):</td>
<td>59.7±3.5</td>
<td>30±1.6</td>
<td>14.4±0.78</td>
</tr>
<tr>
<td>Fluence (J/cm²):</td>
<td>12.3±0.7</td>
<td>12.3±0.69</td>
<td>12.3±0.72</td>
</tr>
<tr>
<td>Intensity (TW/cm²):</td>
<td>24.6±1.4</td>
<td>24.6±1.38</td>
<td>24.6±1.45</td>
</tr>
<tr>
<td>Scan Speed (mm/s):</td>
<td>200</td>
<td>100</td>
<td>24</td>
</tr>
<tr>
<td>Overlap (SPA):</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Sample characterisation was carried out using SEM, optical microscopy and white light interferometry techniques (see section 3.4). To characterise the scribe profile the cross sectioning technique described in section 3.3.4 was used. The processed sample strength was determined using the two point bend test method (section 3.4.4).

Optical ray tracing software (Zemax 12 S/N 33293) was used to determine the effect of polarisation on the propagation of light through the scribed substrate. A V shaped trench with a rounded bottom in a glass substrate was defined using geometric shapes Boolean operators. A linearly polarised Gaussian light source was used to represent the laser. Randomly polarised light was used to represent circular polarisation. The substrate thickness and trench depth were fixed at 100μm and 60μm respectively. Glass properties were loaded from the material catalogue. The beam size to trench width was taken from experimental observations; typically the trench width is slightly smaller than the 1/e² beam diameter. The aspect ratio of the trench was varied by adjusting the trench width. Two million rays were traced through the system. The model assumes the optical properties of the glass substrate are constant. Detectors were placed on the front and rear surface of the glass substrate to detect rays before and after propagation. The detectors were orthogonal to the incident laser beam.
4.4.2 Polarisation Effect

A study on laser scribing of thin glass with a 59.7µm, 30µm and 14.4µm spot diameter linearly polarised beam was performed. For scribes made with a 59.7µm spot, 30 or more passes and polarisation oriented parallel to the plane of incidence (P polarised) damage regions were observed extending away from the trench walls (Figure 4.19). These regions were reduced by decreasing the spot size. Damage to the rear surface is clearly visible in Figure 4.20 for the P polarised case. For S polarised light the damage was notably reduced. Circular polarisation has damage to the rear surface intermediate of the S and P polarised cases. Glass scribed with a 30 µm spot was found to have reduced damage to the rear surface relative to the 59.7µm spot and the 14.4µm spot had no observable damage to the rear surface for both S and P polarised light even with a high number of passes (>300).
Figure 4.19: SEM images showing cross sections of laser scribes in glass. A low pulse energy and high number of passes were used to emphasise the damage for visualisation purposes. Image (a) shows a scribe made by a 59.7\,\mu m diameter P polarised beam with a fluence 5.66 J/cm² and 80 passes, (b) shows a scribe made by a 30\,\mu m diameter P polarised beam with fluence of 8.49 J/cm² and 300 passes and (c) shows a scribe made by a 14.4\,\mu m diameter P polarised beam with a fluence of 12.3 J/cm² and 200 passes.

For 200\,\mu m thick samples damage regions remained visible on the rear surface. Here the damaged regions were further away from the trench as the light must propagate further from the trench wall to reach the rear surface.
Figure 4.20: SEM and optical images showing rear surface damage after scribing with a 60μm spot. Images (a) and (b) show cross sections and rear surfaces of scribes made by a P polarised and S polarised beam, respectively. The samples are tilted by 45°. The rear surface and cross section of the substrate are indicated. The trench is visible in the cross section.

The polarisation of the laser incident on the trench will also be dependent on the laser scanning direction. To illustrate this effect a cross was scribed in a thin glass substrate with fixed linear polarisation.

Figure 4.21: Microscope image showing a plan view of the rear surface of a laser scribed thin glass substrate. The polarisation incident on the trench was varied by altering the scribing direction. The
vertical scribe is P polarised and the horizontal scribe is S polarised. Note the laser scribe is only partially through the substrate.

Thin glass samples were scribed with an increasing number of laser passes with the laser settings from Table 4.1. After 60 passes the S polarised, 59.7μm spot diameter beam had consistently cut through the substrate, the ablation depth is 100μm and the remaining 10μm had fractured (Figure 4.22). The processing speed is 3.33mm/s. In the P polarised case 90 passes are required to achieve a complete cut, giving a processing speed of 2.22mm/s. Scribes made with circular polarisation had ablation depths intermediate of the S and P polarised scribes. A similar test with a 200μm borosilicate glass substrate was performed. Ablation depths were in reasonable agreement with the 110μm substrate. Over 200 passes were required to fully ablate through the 200μm substrate with a 60μm spot and S polarised light.

![Graph showing ablation depth as a function of number of passes for FS IR thin glass ablation. The data points are the average of two or more separate tests. The marked vertical line indicates 60 passes. The aspect ratio for the S polarised 59.7μm spot is 2.2 after 60 passes, for the S polarised 30μm spot the aspect ratio is 3.2 after 130 passes and for the S polarised 14.4μm spot the aspect ratio is 4.3 after 180 passes.](image)

The results of the optical ray tracing model are shown in Figure 4.23. The plots show the intensity distribution at the front and rear surface of the glass substrate for a trench with an aspect ratio of 3. Both tests used an identical substrate and Gaussian light source, except for the polarisation orientation. The corner inserts show the intensity distribution on the rear surface detector; the main images show a cross section through the centre of this intensity
distribution (solid line) and a cross section of the detected intensity at the front surface of the glass (dashed line). The amplitude of the incident Gaussian source on the front surface was reduced by a factor of 2 in the plot for visualisation.

Figure 4.23: Results of optical ray tracing model displaying intensity distribution at the front and rear surface of a glass substrate containing a scribe.

A number of simulations were run to calculate the amount of energy as a function of the aspect ratio. The irradiance cross sections were integrated numerically to determine the amount of energy contained within the incident beam waist after the beam has propagated through the substrate. This was used as a metric to evaluate the magnitude of the polarisation effect (Figure 4.24).
Figure 4.24: Results of optical ray tracing model showing the effect of aspect ratio of the trench on the distribution of energy at the rear surface of the glass substrate.

The profile of the transmitted beam was measured by placing a beam profiler 20mm underneath the sample. The glass was scribed with a 60 µm spot and the settings listed in Table 4.1. The average power of the laser was then reduced to 50mW, well below the damage threshold of the glass. The transmitted beam profile of the stationary laser was detected by the beam profiler (Figure 4.25). The profile of the beam with no sample present was also measured, alternative detector settings were used and so the two plots should not be compared directly.
Figure 4.25: Beam profiles of a low power FS beam transmitted through a scribed glass substrate. The main plots show a cross section through the centre of the energy distribution reaching the detector. The corner insets show images of the energy distribution reaching the detector.

4.4.3 Cut Quality

Full body cuts were made in glass substrates using a 59.7µm spot diameter (1/e²) S polarised beam and the settings in Table 4.1 (Figure 4.26). The glass is completely separated after 60 passes. The cut edge has a taper of 20.3° to the surface. There is no micro cracking or chipping occurring due to the non-thermal nature of the ablation. The quality of the cut face and edge is unaffected by the laser polarisation.
Figure 4.26: SEM image of edge quality of an ultrashort laser full body cut. The sample is tilted by 45°. The left image shows the top surface and the right the rear surface. Some loose debris are visible on the top surface.

The roughness of the cut samples in Figure 4.26 was quantified using an optical surface profiler. The micro voids on the surface caused significant scattering of the light and attenuated the reflected signal returning to the detector. To boost the signal a ~30nm thin gold coating was sputter coated on the sample to increase the reflected signal strength. The cut surface had a Ra roughness value of 407±61nm.
Figure 4.27: Surface profiler measurements of cut edge roughness for a glass substrate cut by full body laser ablation using a FS IR laser. The top image shows a 2D map of the cut edge with the colour scale indicating height. The lower image shows line plots across the sample surface.

Figure 4.28 shows SEM images of the cut face of thin glass samples cut with different applied fluences. A variation in cut surface topography with applied fluence is clearly visible. The full body cuts were produced using a 100kHz repetition rate, a scan speed of 380mm/s and a 59.7μm diameter (1/e²) focused spot. The applied fluence 6.58J/cm², 5.48 J/cm² and 3.68J/cm² for images (a), (b) and (c) respectively. Spot overlap was 95%. The variation in surface topography indicates a change in the material removal mechanism with fluence.
Figure 4.28: SEM images of the cut face topography as a function of applied laser fluence. The applied fluences were 6.58 J/cm², 5.48 J/cm² and 3.68 J/cm² for images (a), (b) and (c) respectively. The laser is incident from the top. The number of laser passes for a complete cut were 10, 30 and 50.

50x10mm samples were produced for a two point bend test. 20 samples were produced. The top surface of the sample denotes the side which the laser is incident on. The bottom surface denotes the opposite side. Ten samples were tested with the top surface facing upwards in the two point bend test and ten were tested with the bottom surface facing upwards. No significant difference in the magnitude of the results was found between the two tests. The results were fitted with a Weibull cumulative distribution and plotted together in Figure 4.29. The 10% failure threshold occurred at 163±2.6MPa.
Figure 4.29: Results of two point bend test on femtosecond IR laser processed willow glass samples. The dashed plot shows the Weibull cumulative distribution with parameters fitted to the measured data. Data points are indicated on the plot. Data was taken with both orientations of the sample. The inserted image shows a sample under inspection in the two point bend test. The image shows the sample immediately prior to fracture. $\sigma_{\text{max}}$ at fracture is 206MPa.

Figure 4.30 shows the effect of applied fluence on ablation depth for a fixed number of passes. The number of passes was fixed at 30, 40 and 50. A 60µm diameter spot was used for all scribes. Scribed samples were cross sectioned and characterised using SEM techniques. The width of the trench increased by approximately 20% with increasing fluence (Figure 4.31). Damage to the rear surface was visible after 30 passes with P polarised light for all fluences and was slightly reduced at lower fluences.
Figure 4.30: Ablation depth as a function of pulse energy for a 60 µm spot diameter. The plotted data is the average of 4 tests and the laser was S polarised relative to the scribe walls. Scribed made with P polarised light showed a similar trend but with ablation depths ~15% lower.

Feature quality diminished at very high fluences (>15J/cm²). Microcracking and significant damage to the rear surface of the glass were visible for high fluences and high number of passes. The taper of the scribe is increasingly non-uniform at high fluences (Figure 4.31).
Figure 4.31: Cross sections of laser scribes in glass at different fluences. The number of laser passes was fixed at 50. Laser is S polarised. Spot diameter was 59.7µm. All other settings are the same as defined in Table 4.1. The applied fluence in each image was (a) 10.6 J/cm², (b) 14.1 J/cm², (c) 17.7 J/cm² and (d) 19.8 J/cm².

4.4.4 HF Etching of Glass

HF etching was carried out as described in section 3.3.6. Glass substrates were scribed using a 60µm spot diameter S polarised beam and the settings in Table 4.1 with 50 laser passes. After the processing the laser scribe was approximately 80µm through the glass substrate. Figure 4.32 (a) shows an SEM image of the rear surface which was pitted due to the HF interaction. Figure 4.32 (b) shows the results of a surface profiler scan on the etched region of the rear surface. The profiler indicates the glass was etched to a depth of approximately 0.3µm. The width of the etched feature is 290µm (FWHM) and the Ra roughness is 48nm.
4.4.5 FS IR Laser Glass Cutting Discussion

Ultrashort laser processing of glass is accurate and deterministic. There is little or no heat affected zone due to the absence of thermal diffusion during the interaction of the laser with the substrate. There is no cracking observed at the cut edge and chipping is minimal (Figure 4.19, Figure 4.26). Due to the deterministic nature of the ablation, femtosecond lasers are suitable for scribing blind trenches, holes or other shallow features in a glass substrate. High density scribing of features is possible due to the negligible heat affected zone.

The damage caused by the scribing process to the rear of the substrate is permanent and visible to the eye (Figure 4.19 and Figure 4.20). This is not only an aesthetic issue, it reduces the energy available for the laser ablation process and potentially reduces glass strength. The damage is similar to that observed by Vanagas et al [69]. Vanagas attributed the damage on the rear surface to stress waves generated by the plasma ablation plume. The experiments were performed using a circularly polarised ultrashort laser, obscuring the polarisation effect.
The considerable reduction in damage to the rear surface of the glass for the S polarised light is strong evidence that the damage is due to optical energy transmission through the side walls of the ablated trench. The higher reflectivity of S polarised light reduces the transmission. The difference in reflectivity can be seen in a plot of the Fresnel equation (57) for glass (Figure 4.33).

\[
R_s = \left[ \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right]^2; \quad R_p = \left[ \frac{n_1 \cos \theta_t - n_2 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right]^2
\]  

(57)

Figure 4.33: Plot of the Fresnel equation (57) for glass. Brewster’s angle is indicated.

The damage is seen only for a high number of laser passes suggesting the damage is due to colour centres or other defects being irreversibly created during successive passes [31, 33] resulting in greater absorption with increasing number of passes. Coloured pigmentation is visible in the rear surface damage on inspection with an optical microscope indicating the possible presence of colour centres. No damage is observed directly beneath the trench as the light from the central part of the beam is heavily attenuated by the surface plasma through absorption and reflection. Decreasing the laser spot size also reduces the amount of visible damage to the rear surface as the angle of incidence, and therefore the reflectivity, of the laser on the trench wall is increased with a smaller spot.

A clear dependence of ablation rate on laser polarisation state can be seen in Figure 4.22. For S polarised light with a 60μm spot diameter the glass was consistently cut through with 60 passes. For P polarised light 90 passes were required to consistently cut through the substrate. A smaller laser spot, 30μm, reduces the amount of visible damage to the rear surface.

-137-
but the polarisation benefit is also reduced relative to the 60\(\mu\)m spot. Results for the 14.4\(\mu\)m spot show that there is no ablation rate benefit to S polarised light over P polarised light. This is counter intuitive as the result of the ray tracing model demonstrates (Figure 4.24). The polarisation benefit should peak with the 30\(\mu\)m spot at an aspect ratio of between 2.5 and 3. The necking visible for the 14.4\(\mu\)m spot scribe in Figure 4.19 indicates that removal of debris is an issue for narrow scribes. Increased roughness of the trench walls caused by debris redeposition also causes the incident laser light to scatter, masking the beneficial effects of S polarised light over P polarised. This will be less of an issue for larger spots as a wider trench provides any particulate ejected from the trench more of an angle from which it can escape from the trench. The non-uniform tapering angle of the 14.4\(\mu\)m spot scribe could also detrimentally impact the processing speed as the reflections may not efficiently couple the energy into the scribe.

The results of the optical ray tracing simulation (Figure 4.23) show that if a 1.74W average power laser beam is incident on a triangular trench of aspect ratio 3 then 96\% of the incident power enters the trench, the rest is reflected away. When the incident light is S polarised, 57\% is confined to the incident focused beam diameter at the bottom of the trench; this corresponds to an applied fluence of 6.72J/cm\(^2\). When the incident laser is P polarised, 45.5\% is confined to the incident focused beam diameter at the bottom of the trench; this corresponds to an applied fluence of 5.37J/cm\(^2\). The decrease in fluence for the P polarised case is due to light being refracted away from the trench walls. Assuming a simple vaporisation model and taking the enthalpy of vaporisation of SiO\(_2\) as 12.3J/g [42] this increase in fluence corresponds to an improvement in ablation depth of approximately 1.36\(\mu\)m per pass. This is in reasonable agreement with experimental results. The model does not account for redeposition of debris.

The transmitted beam profiles (Figure 4.25) provide experimental evidence of the effect of beam polarisation on the energy distribution leaving the rear surface of the glass. S polarised light reduces transmission through the trench walls and consequently increases the fluence in the central part of the profile. The P polarised configuration shows significant intensities to either side of the central peak. The energy transmitted out to the wings may be significantly higher inside the substrate than that which reaches the detector. The incident angle of the transmitted light on the rear surface is close to the critical angle at a glass air interface (\(\theta_c=42^\circ\)) resulting in very high reflectivity and possibly total internal reflection. The light from the
central part of the beam will be incident on the rear surface almost orthogonally and so reflections from the rear surface will have little effect.

The topography of the cut face was strongly dependent on laser fluence (Figure 4.28). At low fluences the surface is spotted with microvoids. As the fluence is increased the presence of microvoids is reduced and the surface has a smoother but still irregular appearance. The change in cut face topography is indicative of the transition from one material removal mechanism to another. At fluences close to threshold slow desorption of material from the sample surface will take place. Voids will nucleate below the surface giving a foam-like surface, similar to what is observed in Figure 4.28. As the fluence is increased phase explosion and Coulomb explosion will become dominant. Phase explosion occurs when the material becomes overheated and undergoes rapid transition to a mixed liquid/gaseous phase with minimal formation of vapour bubbles. Coulomb explosion results in a typically smooth ablated surface. Cut quality is dependent on applied laser fluence with lower fluences giving a smoother and more uniform surface. However, the processing speed is reduced at lower fluences. Optimum laser parameters depending on process requirements can be defined.

The roughness of the cut face showed considerable improvement over the NS ablation regime with the Ra nearly halved. Chipping is reduced overall however some chipping on the rear surface is visible in Figure 4.26. Despite the increase in cut quality the edge strength of the processed glass is shows only a 20% improvement over the NS UV tests.

Increasing the applied fluence further has little beneficial effects on the processing speed. Figure 4.30 shows that as fluence is increased no corresponding increase in ablation depth occurs. For scribes made with 40 and 50 passes we see a decrease in ablation depth. The statistical scatter in the results increases with fluence. For applied fluences greater than 18 J/cm² the increased ablation depth of S polarised light over P polarised light is no longer clear. There is some evidence of beam distortion discussed by Klimentov et al [73] visible in the trench shape for high fluence scribes (Figure 4.31). Increasing the fluence may cause significant ionisation of the ambient air above the interaction zone. This will result in distortion and attenuation of the incident beam causing a decrease in ablation depth.

The HF etching technique increases processing efficiency by using otherwise wasted optical energy to release HF gas which etches the rear surface. There is some collateral etching occurring outside the laser interaction zone which may be problematic for the scribing of high density features. Etch rates are low and the increase in overall processing efficiency is small.
Based on these results a processing window for ultrashort laser processing of thin glass can be identified. A spot diameter of ~60 µm, an applied fluence of ~12 J/cm² and linear polarisation oriented perpendicular to the plane of incidence provided the most time efficient and highest quality cuts. The processing speed (3.33mm/s) is below what would be required for ultrashort lasers to be considered a market disruptor for thin glass cutting. For shape cutting the anisotropic interaction of a linearly polarised laser with the substrate will complicate the process. A motorised half waveplate or a Pockels Cell could be used to quickly rotate the laser polarisation, as the laser goes around the corner of a square for example, so that it is always perpendicular to the plane of incidence. Circular and azimuthal polarisation states interact isotropically with substrates and will not experience this issue. However these states are not ideal, as for circular polarisation the cut quality and speed will be lower than that achievable with S polarised light, while azimuthal polarisation requires costly conversion optics which are sensitive to alignment.

4.5 Conclusions

We have shown the significant differences in cut quality and speed depending on the laser source used. These differences have been attributed to the laser parameters and contrasting absorption mechanisms taking place in the material. Femtosecond lasers offer numerous advantages over conventional short pulse systems due to the extremely short pulse durations employed. Thermal effects and plasma plume shielding can be eliminated, permitting higher quality features to be produced. Nonlinear phenomena such as air breakdown and surface plasma reflectivity will detrimentally impact material removal rates. For laser processing of glass the choice of laser is dependent on process requirements and budget constraints.

<table>
<thead>
<tr>
<th>Laser Process</th>
<th>Processing Speed (mm/s)</th>
<th>Cut Quality (Ra)</th>
<th>Reproducible</th>
<th>10% Failure Stress (MPa)</th>
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<tr>
<td>Desired Parameters</td>
<td>&gt;100</td>
<td>&lt;0.1</td>
<td>✓</td>
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<td>CO₂Vaporisation</td>
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<td>20</td>
<td>79±3.9nm</td>
<td>X</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Laser cutting of thin glass is an emerging technique. The research data presented in this chapter show laser processing is short of the required standard (Table 4.2). Cut quality is reasonable. Full body laser cutting of thin glass is an order of magnitude too slow to be economical in industry despite other advantages of laser processing over mechanical cutting. The high cost of ownership is prohibitive to industrial usage for thin glass processing until an effective process is developed. Laser ablative and vaporisation processes are inefficient. An opportunity exists for a novel approach to the thin glass processing challenge.
In the previous chapter it was shown that full body ablation methods struggle to meet the desired requirements for thin glass cutting. This issue is addressed in this chapter by taking an alternative and novel approach to glass cutting.

5.1 Introduction

Fracture is the fastest and most energy efficient method of cleaving glass. Consider a 500g glass substrate dropped on a hard surface from a height of 200mm. The energy in this system is 1J. This relatively small amount of energy is enough to fracture the glass. The fracture is rapid, typically taking place at speeds of several kilometres per second. The cut face of the glass after fracture is shiny indicating that its surface roughness is on the order of the wavelength of visible light, this edge quality is difficult to achieve by other means. However the fracture in this case is uncontrollable and the substrate will be destroyed. In this chapter methods to control fracture in glass are investigated.

Stress raisers are well studied material features which reduce the fracture strength of brittle materials. Some mechanical cutting wheels use these features to assist in the glass cutting process. Taking inspiration from this, the use of a laser to form stress raising features in a glass substrate will be examined. Lasers are suited to machining microscopic stress raisers in glass due to their flexibility and speed.

The objectives of this chapter are:

- Characterise the speed and quality of commercially available carbide cutting wheels when cutting thin glass.
- Develop an optical beam delivery setup which will allow stress raising features to be quickly produced on a glass substrate.
Investigate techniques for applying tensile stress to the scribed glass.

- Characterise the reliability, speed and quality of the process.
- Analyse the stress field around a stress raiser using the FEM.
- Investigate the potential of this technique as a means for automated thin glass processing at a large scale, integrated into a reel to reel processing platform.

5.2 Mechanical Cutting of Thin Glass

At present there is no published experimental work on the mechanical cutting of ultrathin glass. Initially the feasibility of this process was investigated. The mechanical cutting station described in section 3.3.5 was used to mechanically scribe 100μm and 50μm thick borosilicate glass (Schott AF32). The scribing wheel used was a Bohle cutmaster platinum. The glass was scribed with an applied load of 500g at a speed of 200mm/s. The scribes were fractured by bending the glass sample along the scribe line.

Figure 5.1 shows the results of a mechanical scribe in an ultrathin glass substrate. Figure 5.1 (a) shows the scribe prior to mechanical fracture. Elliptical stress raisers have been produced along the surface. The pressure exerted by the cutting wheel along with the stress raising properties of the ellipses has produced microcracks along the scribe line. The cut face quality of the thin glass substrate can be seen in Figure 5.1 (b). Non-scribed regions are highly uniform and smooth. The region compressed by the cutting wheel shows some deformation. Twist hackles are observed. The quality is adequate compared with full body laser ablative techniques and scribing speeds are high. Cut quality was independent of cutting speed, the maximum achievable speed was limited by the stage movement speed. 20 samples were produced for strength testing using the two point bend test method (see section 3.3.7). 10 samples were tested on the front, scribed surface and 10 were tested on the rear surface. The 10% Weibull failure parameter was 125±6MPa and 119±5.1MPa for the front and rear surface respectively. The plastic deformation of the substrate caused by the scribing wheel has detrimentally affected the edge strength. While this process shows some promising results some fundamental issues remain such as the inability to scribe curves and the incompatibility with a reel to reel processing machine.
Figure 5.1: Images of mechanically scribed and cut 50μm thick glass substrates. Image (a) shows an optical microscope image of a scribed glass substrate prior to fracture. A microcrack extending from each elliptical perforation is visible. Image (b) shows an SEM image of cut face of mechanically processed glass. The perforations due to the serrated edge of the wheel are visible on the edge of the glass.

Taking inspiration from this process an opportunity to use laser produced stress raisers was identified. Substituting a laser for the scribing wheel could potentially improve many aspects of the process. The noncontact nature of the laser may reduce plastic deformation taking place around the stress raisers. A laser process will also enable curvilinear scribing and is compatible with a reel to reel process.

5.3 Optical Design

An appropriate optical setup was determined using optical design software. To achieve an elliptical focused spot asymmetric focusing is required. The simplest optical element for this is a cylindrical lens. A single cylindrical lens will focus the Gaussian laser beam to a narrow line with a length equal to the raw beam diameter. The spot dimensions will be too large for an appreciable laser fluence. The focused spot dimensions must be small enough that the fluence is greater than the damage threshold of the material but the size is balanced against the process speed. A custom lens design was initially considered to achieve the desired spot dimensions. However this design is restrictive, costly and has a long lead time. Instead a telescopic optical arrangement was designed, consisting of a spherical and a cylindrical lens.
Mechanically Inspired Laser Scribing of Thin Flexible Glass

Optical design software (Zemax) was used to determine the required curvature and separation of the lenses. Zemax contains lens catalogues from major suppliers. As a starting point for the design a spherical $f=200\text{mm}$ bi-convex lens and a plano-cylindrical $f=200\text{mm}$ lens were selected from the catalogue. The thickness of the lens was fixed while the separation and curvature of the lenses was set as a variable. An optimization was run to minimise the focused spot dimensions along the $x$ direction. After optimisation the lens curvatures were compared with those available in the supplier catalogues. The closest matching lenses were chosen, an $f=100\text{mm}$ spherical lens (Thorlabs LB1676) and an $f=50\text{mm}$ cylindrical lens (LJ1695RM). The lenses were loaded into the model for further optimisation. In this case all variables were held fixed while the lens separation was variable. The system was again optimised for minimum spot dimensions along the $x$ direction. The working distance of the design is $15\text{mm}$ (Figure 5.2).

![150μm](image)

![25mm](image)

Figure 5.2: Results of Zemax optical design. The main image shows the lens arrangement with the chief and marginal rays drawn. The light propagates through the system from left to right. The left hand lens is the spherical lens. The right hand lens is the plano-cylindrical lens. The insert shows the focused spot dimensions after optimisation. A highly elliptical spot shape has been achieved. Spot dimensions are sufficiently small that the damage threshold of the material can be reached.

An alternative arrangement where a galvo scanner F theta lens is used as the objective lens was also designed. The objective lens used in experiments is a Linos F theta lens ($f=100\text{mm}$). The lens drawings for this lens is proprietary. The example $f=100\text{mm}$ F theta lens from the lens library was used in the model. A similar optimisation procedure to the previous
design was used. The F theta lens dimensions were fixed while the cylindrical lens curvature was set as a variable. The model indicates a long focal length cylindrical lens will give the most suitable spot dimensions, which are approximately twice as large as the fixed lens setup. The closest matching lens available commercially was an f=1000mm lens (Thorlabs LJ1516). A second optimisation was run with the cylindrical lens curvature fixed to determine the lens spacing (Figure 5.3). The working distance of the lens arrangement is 140mm.

![Image of lens arrangement and focused spot dimensions](image.png)

**Figure 5.3:** Results of Zemax optical design. The main image shows the lens arrangement. The chief and marginal rays are drawn. An idealised reflecting mirror was used to direct the beam towards the F theta lens. The insert shows the focused spot dimensions.

### 5.4 Experimental Method

Scribing was performed using an Amplitude Systemes s-Pulse laser with a wavelength of 1030nm and a 500fs pulse duration. The laser had a Gaussian beam profile and emitted a linearly polarised beam. The samples used were 130µm thick borosilicate glass (Corning Willow damage threshold: 3.55Jcm⁻²), 100µm thick borosilicate glass (NEG G-Leaf glass, damage threshold: 3.13Jcm⁻²) and 330µm thick sapphire (crystal photoelectric material,
Mechanically Inspired Laser Scribing of Thin Flexible Glass

damage threshold: 5.04Jcm\(^{-2}\)). As shown in the previous chapter polarisation of the incident laser is an important consideration when processing thin transparent materials with ultrashort lasers. A half waveplate was placed in the beam path, prior to the focusing optics, to rotate the plane of polarisation. The laser polarisation is important in recess formation, but the dependence is less clear due to the astigmatism introduced into the system by the asymmetric focusing optics.

![Image](image.png)

**Figure 5.4: Illustration of beam delivery system and sample placement for fixed lens setup. The lens tube containing the optics was screwed into the rotary stage. The inserted image shows an SEM image of a percussion drilled recess in a borosilicate glass substrate.**

For the fixed lens setup the lenses were mounted in a lens tube at the prescribed separation (Figure 5.4). Focusing optics were arranged as discussed in section 5.3. A short working distance, ~15 mm, means debris extraction is essential to prevent contamination of the objective lens. An air extract was used to reduce the amount of emitted material depositing on the lens. The Rayleigh length of this configuration is approximately 0.4 mm. The maximum power tolerance of the configuration was limited (<2W), as the cylindrical lens is close to the focus of the spherical lens. Several lenses were damaged after use with high power pulses, with dark spots visible in the bulk of the glass.

Focused spot dimensions (1/e\(^2\)) are 130μm and 32.5μm for the major and minor radii respectively, measured using a beam profiler (Ophir) (see Figure 5.5). To scribe curves the elliptical spot most be rotated to follow the arc of the curve at every point. This can be achieved
by rotating the elliptical laser spot or rotating the sample relative to the spot. In the present setup the lens tube was fixed to a CNC rotary stage allowing synchronised control (see section 3.3.2). The required rotation between points is dependent on the radius of curvature of the desired curve.

Figure 5.5: Focused spot dimensions of the fixed lens setup in Figure 5.4, measured using a beam profiler (Ophir). Vertical and horizontal orientations of the elliptical spot are shown. The cylindrical lens was rotated 90° between images.

For the galvo scanner F theta lens setup the cylindrical lens was arranged in the beam path prior to the galvo entrance aperture (Figure 5.6). With this configuration the elliptical spots with slightly larger dimensions than the fixed lens setup. Focused spot dimensions (1/e²) are 143μm and 64μm for the major and minor radii respectively, measured using a beam profiler (Ophir). The spot dimensions are considerably smaller than predicted in the optical model Figure 5.3. The discrepancy between measured and predicted spot dimensions is attributed to approximations of the proprietary F-theta lens dimensions. The focused spot shape is undistorted across the field of view (75mmx75mm) of the scanner. Curvilinear scribes were not attempted with this setup.
Figure 5.6: Illustration of beam delivery system and sample placement for galvo scanner setup. The insert an optical microscope image of a percussion drilled elliptical recess in a borosilicate glass substrate.

Samples were fractured along the scribed line by applying a bending stress using a two point bend test (TPBT) apparatus (see section 3.4.4). The samples were bent along the scribe path applying a bend stress to the scribe. The bend stress will have a large tensile component on the upper, outer surface. The sample was oriented so that the scribe was on the upper surface in the test. The force required to fracture the scribed substrate was determined from the test. Fracture of curvilinear shapes is more complex, additional bending steps were required to apply stress to each side of the shape. Alternatively the stress was applied thermally. Scribes were locally heated using a focused CO$_2$ laser. The laser power is set sufficiently high to heat but not melt or vaporise the material. The laser spot is followed by coolant to induce tensile stress and fracture along the line defined by the ellipses. Coolant was applied to the sample after heating using a vortex tube coldstream air gun (Meech). The vortex tube outputted air with a temperature of approximately -5°C. Ambient cooling will also lead to tensile stress.

### 5.5 Thin Glass Processing

This section examines scribing and fracturing of thin borosilicate glass substrates using the mechanically inspired process.
5.5.1 Thin Glass Scribing

The laser configuration outlined in Figure 5.4 was used to percussion drill blind recesses with a centre to centre separation of 0.4mm in borosilicate glass substrates. Figure 5.7 (a) shows borosilicate glass samples irradiated with a pulse energy of 180μJ and 250 pulses per spot at a repetition rate of 10kHz. The fluence was 2.7Jcm⁻², sufficient for multi-pulse ablation [152]. The recesses are uniform and well defined with no microcracking occurring in the surrounding material.

For recesses irradiated with >500 pulses per spot, non-linear microcracks at the tip of the ellipse were observed (Figure 5.7 (b)). The cracks extended from the tip of the ellipse towards the next ellipse in the scribe. The crack merges with the crack from the subsequent ellipse. The crack was nonlinear, with micrometer scale deviations from the straight line defined by the ellipses. Conjoined cracking occurred for spot separations up to 1mm. Crack bifurcation is also observed. The cracks can be extended and driven into the material by locally heating the substrate. A focused (162μm 1/e² diameter) CO₂ laser with 8W of power at 10kHz was scanned across the scribed glass at 50mm/s. The laser power was sufficient to heat but not melt the substrate. Ambient, passive cooling was sufficient to propagate the cracks. Part drop out does not occur, however only a negligible amount of force is required to separate the glass. Light handling of the glass is sufficient to complete the cut. The cut edges occasionally deviate from the defined path by up to 1mm when crack bifurcation occurs.
Figure 5.7: Optical microscope images of processed willow glass samples. (a) Image of a row of elliptical recesses on the glass surface, scribed with 250 pulses per spot at a separation of 0.4mm. (b) Image of a row of elliptical recesses on the glass surface, scribed with 700 pulses per spot. Microcracking and crack bifurcation is observed. The microcrack is conjoined with the next stress raiser.

Samples were processed using the galvo scanner setup shown in Figure 5.6. Spot dimensions were smaller than predicted in the optical design Figure 5.3. The width of the recess was too large to produce effective stress raisers. The applied laser fluence was low and resulted in inconsistent sample processing.

5.5.2 Cut Quality

The scribe in Figure 5.7 (a) was fractured by applying a bend stress using a two point bend test. A bend stress of 110MPa was required to fracture the scribe. Figure 5.8 shows SEM images of the cut edge. There was some small localised deviation from the defined plane of cleavage. There are apparent similarities with the sample cut with a mechanical cutting wheel shown in Figure 5.1 (b).
Figure 5.8: SEM images of straight line scribed willow glass samples after fracture. Samples tilted by 45°. Image (a) shows the top surface of the glass after fracture. Glass is shown as processed, some loose debris is visible on the top surface. The elliptical laser ablated recess is visible and extends 22μm into the depth of the substrate. Image (b) shows the bottom surface of the glass.

The cut face roughness was measured using a surface profiler (Figure 5.9). Typically surfaces produced by brittle fracture have low roughness. Due to the low roughness the reflected signal was strong and no gold coating was required. The surface profiler measured an Ra roughness value of 18.2±2.5nm. This figure does not include measurements taken from the elliptical recesses, only the region between.
Figure 5.9: Surface profiler measurements of cut edge roughness for a glass substrate cut by mechanically inspired laser scribing process. The sample was fractured by applying a bend stress. The top image shows a 2D map of the cut edge with the colour scale indicating height. The map is centred on the region between the elliptical notches. The notches are visible on either edge of the map. The lower image shows line plots across the sample surface. The average Ra value from these line plots is 18.2nm.

Post processing techniques can be applied to the cut edge to improve edge quality. Edge reflow by heating using CO2 laser was used to reduce the non-uniformities around the elliptical recesses. The sample was preheated in a MUFLA oven at 470°C to reduce thermal shock in the glass during laser heating and subsequent cooling. The edge was heated using a CO2 to a temperature above its melting temperature but below its boiling temperature. A focused (162μm 1/e² diameter) CO2 laser with 12W of power at 20kHz repetition rate, was scanned across the scribed glass at 100mm/s. The melted regions reflowed and smoothed the non-uniformities along edge (Figure 5.10).
5.5.3 Strength Testing

The strength of processed samples was measured using the two point bend test method (see section 3.4.4). The samples were scribed on all sides using the described method and fractured by applying stress using a two point bend test. The dimensions were 50x10mm. Fracture was recorded using a high speed camera to allow precise determination of the bend stress at the moment of failure (Figure 5.12). A sample group of 25 was tested, 10 on the front surface (laser processed side) and 15 on the rear unaffected surface. The rear side of the sample was found to have a higher fracture strength than the front side. The data was fitted with a two parameter Weibull cumulative distribution (see section 3.3.7). Based on this analysis the stress at which 10% of samples will fail was determined, 98±11.5MPa for the front and 202±19.5MPa for rear surface (Figure 5.11).
Figure 5.11: Results of a two point bend test performed on mechanically inspired laser processed Gleaf glass samples. The dashed plots show the Weibull cumulative distribution with parameters fitted to the measured data for the front and rear surface. Data points are indicated on the plot. The 10% failure stress is indicated by a dotted line.

Figure 5.12 shows a processed glass sample under inspection in a two point bend test before and after failure. The maximum bend stress is determined from equation (50). For Figure 5.12 (a) the contact angle is 0° and the plate separation is 22mm when fracture occurred, giving $\sigma_{\text{max}}=438\text{MPa}$.

### 5.5.4 Fractography

Figure 5.12 (b) shows the glass after the fracture event. The sudden release of bend stress produces a large number of glass fragments of various size. It is overly onerous, in this case, to attempt to pinpoint the origin of the fracture. Consequently it is not possible to observe the fracture surface. To give an indication of the origin of the fracture, the two point bend test setup was reconfigured so that the high speed camera recorded the fracture form above. A 50x10mm Gleaf borosilicate glass sample was produced as before and placed under an increasing bend stress until failure. Using this setup the fracture pattern $\sim150\mu\text{s}$ after fracture was recorded (Figure 5.12 (c)).
To measure the speed of the propagating crack a 95kHz high speed recording of the fracture process was taken (Figure 5.13). At this recording rate the image resolution is reduced to 256x128. The recording was taken with a top down viewing angle. The zoom of the objective lens was adjusted to its maximum setting to compensate for the low resolution. The increased zoom and reduced exposure (8μs) placed demanding requirements on sample illumination. The floodlights were set to maximum brightness and the camera gain increased to achieve an appreciable signal. Crack propagation was not visible in the recording, the time taken for the crack to propagate across the sample was less than the time between frames in the recording (10.5μs). Taking the field of view of the lens and the time between frames into account, the crack was propagating at a speed of at least 267m/s.
Figure 5.13: Stills from a 95kHz high speed recording of fracture in a scribed thin glass sample. The top surface of the glass is shown in the image, with the scribe visible. Image (a) shows the sample immediately prior to fracture. Image (b) shows the sample 10.5μs later. The sample has fractured along the scribed line.

5.5.5 Curved Scribes

Figure 5.14 shows curvilinear scribes produced in borosilicate glass. The curves were scribed by rotating the cylindrical lens along an arc while the laser was scanned in a curved path (Figure 5.14 (a)). The separation of the ellipses was reduced to 0.3mm to improve the consistency of the curved cut edge. The major axis of the ellipse was parallel to the tangent of the curve at each point. The borosilicate samples were fractured using mechanical force. Each side of the shape was fractured independently. There was some micrometer scale non-uniformities along the cut edge due to the finite size of each elliptical recess (Figure 5.14 (b)). With this method it was possible to scribe curves with radii of curvature of 5mm (Figure 5.14 (c)).
Figure 5.14: Optical microscope images of curved samples. Image (a) shows the front surface of a willow glass substrate prior to fracture. The scribe is curved with a 5mm radius of curvature. Image (b) shows the front edge of a curved sample after fracture. Some micrometer scale non-uniformities are visible. Image (c) shows a camera image of two curvilinear scribed borosilicate samples after mechanical fracture, radius of curvature is 5mm and 10mm respectively.

5.5.6 Polarisation Effect

As shown in the previous chapter the polarisation of the incident laser will affect the transmission of the laser through the sample during processing of transparent materials. Due to incubation effects, the transmitted energy will lead to damage regions on the rear surface of the material after multiple pulses. Figure 5.15 shows similar effects were observed when percussion drilling elliptical craters in the present work. In this case the damage to the rear surface was strongly dependent on the orientation of the elliptical spot. Rotating the plane of polarisation using a half waveplate had little effect.
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Figure 5.15: Optical microscope image of the rear surface of a Willow glass substrate after percussion drilling elliptical recesses. The positions of the ellipses are marked with a dashed line. Laser polarisation is indicated. The laser polarisation was rotated between recesses. Image (a) shows horizontally oriented recesses, image (b) shows vertically oriented recesses. The damage regions are reduced for the vertical orientation.

5.5.7 Discussion

The spontaneous fracture observed after high pulse irradiation is likely due to thermal stresses induced during the laser interaction and stresses induced in the material during optical breakdown. Recoil pressure from species leaving the glass surface acts on the non-ablated material due to conservation of momentum. These stresses combined with the stress concentration at the tip of the ellipse is sufficient to form a crack in the material. Cyclic fatigue due to heating and cooling cycles may be lowering the material strength and contributing to the spontaneous fracture. True brittle materials will not deform plastically and therefore will not experience cyclic fatigue. Authors have observed cyclic fatigue in some glass materials[153, 154]. Microcracking is a desirable feature of the process however when processing silica based glass we also have crack bifurcation occurring. Crack bifurcation is an unpredictable process. Edge cracks will catastrophically reduce the strength of the processed glass. Reducing the pulses per spot to 250 prevents stray fracture occurring due to the reduction in thermal build up (Figure 5.7).

The discrepancy between the predicted spot dimensions in the galvo scanner setup and the experimentally observed spot is likely due to the F theta lens used in the model. No structural information regarding the Lions F theta lens used in experiments was available. The lens used was an example lens from the lens library and may have design differences. Further
Mechanically Inspired Laser Scribing of Thin Flexible Glass

Optimisation of the model indicates that a reduced input beam diameter will reduce the focused spot dimensions. A beam reducer setup prior to the cylindrical lens may give a reduced spot and a more effective process.

The cut quality and scribing speeds achieved in the straight line cuts compare favourably with laser ablation and mechanical glass cutting techniques. For borosilicate samples the scribing speed is 11.4 mm/s due to the 25 ms dwell time per spot, 10 ms stage movement time and the 0.4 mm spot separation. The samples in Figure 5.8 were fractured using mechanical force supplied by bending the sample. A chopper bar could be used as a more consistent alternative to supply this force along the scribed line. The cut face is highly smooth (Ra=18.2 nm) as expected from a fractured brittle substrate. The imperfections caused by the laser interaction can be reduced by applying a thermal reflow treatment (Figure 5.10). Thermal fracture of scribed substrates is an attractive option for cleaving scribed substrates. Thermal fracture must be initiated by a pre-existing defect or microcrack. The microcracking occurring after glass scribing with >500 pulses per spot is nonlinear and nonuniform leading to millimetre scale deviations in the cut edge after thermal fracture.

The two point bend test (Figure 5.11) of the borosilicate samples, after scribing and mechanical fracture, showed the rear surface had significantly higher edge strength than the top surface. A sample placed in a two point bend test will experience a tensile stress in the upper surface, while the lower surface will experience a compressive stress. The laser notches produced on the glass surface will amplify any tensile stresses and cause the glass to fail at a lower bend stress. When the notches are on the lower surface a higher bend stress can be achieved as the notches experience compressive stress which is not amplified and will not weaken the substrate. The fracture strength of the processed glass is comparable to mechanical cutting and laser ablative processes.

Table 5.1: Table comparing the processed edge strength of thin glass cut using various laser and mechanical processes. Laser processing results are taken from the previous chapter. The number indicated is the 10% failure rate calculated from the Weibull cumulative distribution

<table>
<thead>
<tr>
<th>Processing Method</th>
<th>CO₂ Laser</th>
<th>NS UV</th>
<th>FS IR</th>
<th>Mechanical Cutting Wheel</th>
<th>Mechanically Inspired Scribing</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Failure Stress (MPa)</td>
<td>155±9</td>
<td>136±2.8</td>
<td>163±2.6</td>
<td>125±6</td>
<td>202±19.5</td>
</tr>
</tbody>
</table>
Fractographic analysis on fracture surfaces was difficult due to the large amounts of fragments produced in the fracture event Figure 5.12. Pinpointing the origin of fracture is impractical and onerous. Figure 5.12 (c) shows the surface of the glass substrate 150μs after fracture. The cracks are radiating from a point on the top edge of the sample. This indicates the sample failed due to an edge defect. The defect was most likely micrometer scale chipping at the edge of the sample, caused by the laser scribing process or the mechanical fracture step. Chipping at the edge of the sample will act like stress raising defects when a tensile stress is applied causing the substrate to fracture. In an attempt to measure the speed of the propagating crack a high speed recording at 95kHz of the fracture process was taken. Even at such at high frame rate the propagation of a crack is too fast to measure. It was concluded that the crack must be propagating at a speed of at least 267m/s. Techniques such as high speed photography, ultrasonic and electrical grid methods have been used to measure the propagating crack tip velocities in brittle materials [115-117]. Typically values between 1-3km/s are observed. A high speed recording with at least 500kHz frame rate would be required to detect this crack propagation. The high speed camera used in this work can operate at 500kHz, however image resolution and lighting is limited.

Figure 5.14 shows curvilinear scribes and processed samples. For a 5mm radius of curvature the rotation between spots is 5.1°. The spot separation was reduced to 0.3mm on curved parts to allow more control over the crack. Due to the low rotation speed of the rotary stage (23deg/s) the jump time is 220ms. Consequently the processing speed for curved scribes is reduced to 1.22mm/s. Depending on the shape two or more mechanical fractures are required to remove the scribed part from the bulk substrate. Cut quality on curved parts is similar to straight sections. Some micrometer scale deviations are visible along the cut edge in Figure 5.14 (b). During fracture the crack will propagate from one ellipse to the next in a straight line. As a result the curve is essentially an approximation made up by a series of small straight sections. To improve uniformity a greater number of elliptical spots with smaller dimensions could be produced in the scribe. This will diminish the tendency of the crack to deviate. Additional optical elements are necessary to reduce the spot dimensions.

After scribing damage regions similar to those observed in the previous chapter were seen on the rear surface of the glass substrate (Figure 5.15). The orientation of the elliptical spot affected the amount of damage, with vertical orientation giving reduced damage compared with horizontal orientation. Rotation of the plane of polarisation had a negligible effect on the observed damage, contrary to the conclusions from chapter 4. It was initially thought that there
was an issue with the optical alignment of the system, however the preference for one orientation over the other remained after several realignment attempts for both the fixed lens and galvo scanner systems. The optical model indicates the polarisation is unchanged by propagation through the system for both the fixed lens and galvo scanner system. A cylindrical lens has two foci, the sagittal focus and the transverse focus. This asymmetric focusing may be manipulating the plane of polarisation making it difficult to define the polarisation incident on the sample. It has been demonstrated that a pair of identical cylindrical lenses separated by twice their focal length can be used as a mode converter for a collimated Gaussian input beam[155]. The effect of a single cylindrical lens and a spherical lens on the polarisation is an open question.

5.6 Sapphire Processing

This section examines the mechanically inspired scribing technique applied to sapphire processing.

5.6.1 Sapphire Processing Results

The technique described in the previous section was applied to sapphire substrates. The fixed lens setup outlined in Figure 5.4 was used to scribe 330μm thick sapphire substrates with a laser pulse energy of 180μJ and a repetition rate 10kHz. Figure 5.16 shows curved scribes produced using 400 laser pulses per spot. Microcracking at the tip of the recesses is visible, as was the case with borosilicate glass. Significantly in this case the microcrack is more linear with no crack bifurcation occurring. The cracks can be extended and driven into the material by locally heating the substrate. A focused (162μm 1/e² diameter) CO2 laser with 8W of power at 10kHz was scanned across the scribed glass at 50mm/s. The laser power was sufficient to heat but not melt the substrate. Passive ambient cooling was sufficient to propagate the cracks. A negligible amount of mechanical force was then required to separate the substrate. The microcracking is similar to that observed after scribing with a mechanical cutting wheel (Figure 5.1 (a)).
5.6.2 Sapphire Processing Discussion

For sapphire samples microcracking is occurring at the tip of the elliptical stress raiser for >400 pulses per spot. The microcracking in this case is linear and crack bifurcation is not occurring. Consequently processed sapphire substrates are suitable for thermal fracture. Applying stress thermally is preferable as it is a more accurate and repeatable process compared with mechanical stress. Thermal fracture is also faster and readily automated. Sapphire samples are less susceptible to stray fracture, relative to borosilicate samples, due to a larger elastic modulus (400GPa and 70GPa respectively[110]). A simple calculation on the Rayleigh wave speed shows the terminal crack velocity \( v_T = \sqrt{E/\rho} \) in sapphire is approximately 1.96 times greater than in borosilicate glass. Consequently we observe a significant reduction in stray fracture for sapphire samples. The crack velocity does not reach a sufficiently high value for dynamic effects to occur. As the crack passes through an elliptical defect, the stress field around the ellipse will perturb the crack propagation reducing the velocity. Reducing the crack velocity is beneficial as it lowers the risk of crack bifurcation occurring.
5.7 Mechanical FEM Analysis

The stress field around an elliptical defect in a brittle plate was simulated using the FEM (COMSOL). Analytic solutions for the stress field in a loaded substrate typically involve complex mathematics even for simple configurations. COMSOL utilises the FEM to produce numerical solutions to physical problems (see section 3.5.2).

5.7.1 Model Details

The solid mechanics module was used for this model. This module first solves for the stress distribution based on input displacements and loads. The resulting stress tensor from a tensile edge load being placed on a 2D plate was calculated.

The model calculates the stress tensor by evaluating the material displacement at each discretised element for the prescribed load. The model treats the substrate as a linear elastic material. Relevant material properties for borosilicate glass were loaded from the material library. The relationship between stress ($\sigma$) material displacement ($u$) and applied load ($F$) is given by: ($\nabla \sigma = \rho \delta^2 \frac{\partial u}{\partial t^2} - F$). All boundaries, except those with an applied load, were designated free.

![Figure 5.17: Results of COMSOL modelling of stress concentration factor in a 2D plate containing an elliptical hollow under tensile stress. The stress concentration factor was found by calculating the stress tensor along the y axis and normalising this to $\sigma_\infty$. Main image shows the stress concentration factor in](image)
the entire plate. The inserted plot shows a line plot of the stress concentration factor through the centre of the ellipse parallel to the major axis.

5.7.2 Discussion

The FEM analysis (Figure 5.17) shows reasonable agreement with the Inglis formula for the stress concentration factor at the apex of the ellipse \( K=2a/b \). For an ellipse with \( a=106\mu m \) and \( b=14.9\mu m \) we have \( K=14.2 \). This is in reasonable agreement with the FEM model which indicates \( K=18.5 \). We also see that \( K \) diminishes to almost unity at a distance \( \sim a \) from the tip of the ellipse. This indicates that stress raiser separation will be an important consideration in the fracture process.

5.8 Conclusions and Future Development

The laser source used was restrictive to the overall processing speed. The pulse energy required for glass processing (180\( \mu J \)) was available only at low repetition rates (10kHz). Ideally a 200 kHz 50W ultrashort pulse laser would be used giving straight line processing speeds of \( >>500mm/s \). For curved cuts high speed rotation of the spot to complement the high galvo scanner speed is envisaged with additional optoelectronic equipment. Air bearing rotary stages with rotation speeds of \( 4800\text{deg/s} \) are available. Alternatively substituting the mirror immediately before the galvo scanner with a deformable mirror or DMD could allow one dimensional focusing and also rapid rotation of the beam shape.

As discussed in the introduction any sharp corner will concentrate tensile stresses. A variety of alternate shapes are envisaged depending on the requirement. For example a crescent shaped recesses for processing corners and a 3 pointed triangle to initiate fracture along more than one plane. A spatial light modulator could be used to allow dynamic and flexible laser focusing conditions. This method is applicable to materials such glass, ceramics and metals processed below the ductile to brittle transition temperature. The ductile to brittle transition temperature in steel is typically \(-50^\circ\text{C} \) [3], dependent on the carbon content. A ductile material which has a tensile stress applied rapidly compared with the characteristic relaxation time of the constituent atoms will exhibit brittle behaviour[122].
A key advantage of the mechanically inspired scribing technique is the compatibility with galvo scanners. This allows high speed scanning of the laser without the need for sample translation and enables easy integration into pre-existing systems. The low NA of the focusing optics mean the process has a large working distance and Rayleigh range. This compares favourably with filamentation processes (see section 2.2) which require tight focusing from high NA microscope objectives.

An alternative process for producing curvilinear controlled fracture in thin brittle materials has been demonstrated. This method is founded in fracture theory and borrows from well-established mechanical cutting methods. This process is faster and produces higher quality cuts than mechanical and laser cutting equivalents. A patent has been filed to protect this technique and allow further commercial development (see section 1.5). The process has more flexibility than filamentation methods and is applicable to a wider range of materials. Implementation of this technique in a reel-to-reel manufacturing line, while challenging due to the bending requirement, is feasible given the line tension and bend stresses intrinsic to the reel-to-reel process. This challenge will be examined in the next chapter.

Figure 5.18: Diagrams showing possible alternative shapes for the mechanically inspired scribing process. Image (a) shows a crescent shape which could be used to direct a crack around a tight curve. Image (b) shows triangle which can initiate fracture in three directions.
Chapter 6
Controlled Fracture of Scribed Substrates through Mechanical Resonance

The previous chapter outlined a new processing technique for thin flexible glass which uses tensile and bend stresses in glass to cause controlled fracture. In this chapter an alternative technique to fracture a scribed substrate is investigated to improve the suitability of the mechanically inspired scribing process in industrial environments. Mechanical resonance is used to produce a bending stress in the glass which will fracture the scribe if the stress is sufficient.

Resonance is a phenomenon in which a system will oscillate at a particular frequency when driven by a periodic external force. The system will have a maximum amplitude response when the driving force is at a characteristic frequency of the system, known as the resonant frequency.

6.1 Introduction
Resonance will occur when a system is able to store energy from a periodic external force and convert energy from one source to another, typically kinetic to potential energy. Energy lost during this conversion process is called damping. The amplitude of the oscillation will increase with each cycle as the system stores the vibrational energy. If the driving force were removed a damped oscillator will eventually halt. There are many examples of resonance such as the increasing amplitude of a child on a swing pushed periodically at the swings natural frequency or a rattle in a car engine which occurs only at a certain rpm value. Electrical resonance will occur in an LC circuit if an AC current is applied at a particular frequency. Energy will oscillate between the electric field of the capacitor and the magnetic field of the inductor. Oscillations are damped by electrical resistance in the circuit.
Controlled Fracture of Scribed Substrates through Mechanical Resonance

If a system is driven at frequencies other than the resonant frequency it is referred to as forced oscillations. For a sinusoidal driving frequency \( f_d \), and assuming the displacement is related to the driving frequency, the relationship between the oscillation amplitude \( A \), and the applied force \( F \) is given by (58). \( \gamma \) is the damping term, \( k_s \) is the effective spring constant of the system and \( m \) is the mass [156].

\[
A = \frac{F}{\sqrt{(k_s - mf_d^2)^2 + \gamma^2 f_d^2}}
\]  

(58)

Figure 6.1 shows a plot of (58). The amplitude has a maximum value when \( k_s - mf_d^2 = 0 \), thus the resonant frequency is given by \( f_R = \sqrt{k_s/m} \). For \( f_d = 0 \) we have an amplitude \( F_A/k_s \), this corresponds to the displacement due to a constant applied force. A lightly damped system exhibits a sharp peak in amplitude when \( f_d \) is close to \( f_R \). Increasing the damping in the system will cause the peak to reduce in height, broaden and move towards a lower frequency (see Figure 6.1). A heavily damped system will have a nearly uniform frequency response.

\textbf{Figure 6.1: Plots of expression (58) for a range of damping values.}

In this case the oscillating system is a glass substrate and we have mechanical resonance occurring. The resonant frequency is dependent on sample dimensions, density, elastic modulus and constraints. If the damping in the system is small the resonant frequency approximates the natural frequency. The oscillations will cause a bending stress in the glass which will be a maximum at the apex of the bend. The stress will be tensile on the upper surface.
of the curve and compressive on the inner surface of the bend, similar to the two point bend test. If a surface containing a surface stress raiser is oscillating the tensile stress in the bending surface will be concentrated at the tip of the ellipse. If the amplitude of the oscillation is sufficient the substrate will fracture along the lines scribed by the ellipse.

6.2 Resonant Frequency and Mode Shape

In this section the resonant frequency and mode shape of an oscillating fixed glass substrate is determined using analytical and FEM techniques.

6.2.1 Analytical Solutions

The glass plate is essentially a vibrating beam and so classical beam theory can be used to analyse the vibrations and mode shapes. Beams are a fundamental construction component in buildings and so have been comprehensively analysed by structural engineers. The Euler-Bernoulli beam model is a classical theory which can be used to provide analytical solutions for the resonant frequency and mode shape. For a homogeneous beam the dynamic Euler-Bernoulli equation of motion is given by (59). This expression is derived by considering the strain energy due to bending and the kinetic energy due to lateral displacement. $\omega$ is the angular velocity of the beam, $q$ represents potential energy due to any external load, $\mu$ is the mass per unit length, $E$ is the elastic modulus and $I_A$ is the beam area moment of inertia[157]. The model assumes that the axial dimensions are much larger than the other beam dimensions, the material obeys Hooke’s law and Poisson’s ratio is assumed to be zero.

\[
EI_A \frac{\delta^4 \omega}{\delta x^4} = -\mu \frac{\delta^2 \omega}{\delta t^2} + q \tag{59}
\]

To solve this expression we assume the beam is freely vibrating ($q=0$). The displacement function can be separated into time and space functions $y(x,t)=Y(x)T(t)$. Inserting this expression into equation (59) produces expression (60). Partial derivatives have been replaced with total derivatives as $Y$ only depends on $x$ and $T$ only depends on $t$.

\[
EI_A/\mu Y(x) \frac{d^4 Y(x)}{dx^4} = -1/T(t) \frac{d^2 T(t)}{dt^2} \tag{60}
\]
As the left hand side of (60) depends only on $x$ and the right hand side depends only on $t$ we can solve this equation using the method of separation of variables. Consequently both sides of the equation (60) can be set equal to the same constant ($\omega$).

$$ \frac{d^4Y(x)}{dx^4} \frac{\mu \omega Y(x)}{EI_A} = 0; \quad \frac{d^2T(t)}{dt^2} + \omega T(t) = 0 \quad (61) $$

The general solution for the spatial function, $Y(x)$, can be found by eigenfunction expansion (62). This equation defines the mode shape, where $\lambda = \mu \omega / EI_A$. $\lambda$ is the dimensionless wavenumber and represents $1/2\pi$ times the number of cycles in the beam length. The $C$ constants are determined from the beam boundary conditions.

$$ Y(x) = C_1 \cosh(\lambda_n x) + C_2 \sinh(\lambda_n x) + C_3 \cos(\lambda_n x) + C_4 \sin(\lambda_n x) \quad (62) $$

Different boundary conditions are applied depending on the particular beam configuration. For a beam of length $L$ with both ends fixed we apply the boundary conditions that $Y(0)=Y(L)=0$ and $Y'(0)=Y'(L)=0$ to equation (62). These boundary conditions require that $C_2=-C_4$ and $C_1=-C_3$. Writing the expression for $Y(x)$, $Y'(x)$ and the $C$ constants as a matrix with a determinant of zero the nonzero solutions are of the form given in equation (63).

$$ \cosh(\lambda_n L) \cos(\lambda_n L) = 1 \quad (63) $$

The roots of this equation can be calculated numerically using the variational iteration method. The first three roots are $\lambda_{1,2,3} L = 4.73, 7.85, 10.9$ [158]. The formula for the resonant frequency is found by rearranging the given expression for the wavenumber (64). $I_A$ is the area moment of inertia of the beam. For a rectangular beam cross section $I_A = bh^3/12$ where $b$ and $h$ are the width and height of the beam cross section. Typically the samples we are processing have dimensions $b=10mm$, $h=0.1mm$ and $L=50mm$ with $\mu=2.52g/m$. Using equation (64) the resonant frequency for this system is 220Hz.

$$ f_n = \frac{1}{2\pi} (\lambda_n L)^2 \sqrt{\frac{EI}{\rho AL^4}} \quad (64) $$

To determine the mode shapes we again consider equation (62) with the boundary conditions $Y(0)=Y(L)=0$ and $Y'(0)=Y'(L)=0$. $C_1$ is an independent variable which can take many values. If we assume $C_1=1$ we can rearrange (62) and express the rest of the $C$ constants as (65).

$$ C_1 = 1, C_2 = \frac{\sinh(\lambda_n L) - \sin(\lambda_n L)}{\cos(\lambda_n L) - \cosh(\lambda_n L)}, C_3 = -1, C_4 = -\frac{\sinh(\lambda_n L) - \sin(\lambda_n L)}{\cos(\lambda_n L) - \cosh(\lambda_n L)} \quad (65) $$
Inserting these expression into equation (62) provides an expression for the mode shape. Using the $\lambda_n L$ values determined numerically from equation (63) the mode shapes can be plotted (Figure 6.2).

$$Y(x) = \sin \lambda x + \left( \frac{\sinh \lambda L - \sin \lambda L}{\cos \lambda L - \cosh \lambda L} \right) \cos \lambda x - \sinh \lambda x - \left( \frac{\sinh \lambda L - \sin \lambda L}{\cos \lambda L - \cosh \lambda L} \right) \cosh \lambda x$$  \hspace{1cm} (66)

![Mode Shapes Plot](image)

Figure 6.2: Plot of equation (66) showing the first 3 mode shapes of a freely oscillating beam with both ends fixed.

The Euler-Bernoulli beam model tends to overestimate the natural frequency of a beam by up to 26% [159]. This error is reduced for slender beams, which is certainly the case here. An FEM analysis on the same system was performed to provide independent verification of the resonant frequency and mode shape.

### 6.2.2 FEM Analysis
The resonant frequency and mode shape in a glass plate was determined using the FEM (COMSOL). The mode shape was then used to determine the bend stresses in the deformed substrate. Analytic solutions for the stress field in a loaded substrate typically involve complex mathematics even for simple configurations. COMSOL utilises the FEM to produce numerical solutions to physical problems (see section 3.5.2).
The solid mechanics module was used for this model. A 3D geometry was defined and meshed as discussed in section 3.5.2. The eigenfrequency solver was used to determine the eigenfrequency of the system. When using the solid mechanics physics module the eigenfrequency calculates the natural vibrational frequencies of the system. The eigenfrequency solver is an iterative solver. When the geometry is discretised the eigenvalue system can be written in a generalised form as (67). The solver attempts to linearise the problem about the solution vector $U_0$ by evaluating $E$, $D$, $K$ and $N$. $E$ is zero for linear problems, such as this, where the variables are independent of the solution. $\lambda_E$ is the eigenvalue, $\lambda_0$ is the linearisation point and $\Lambda$ is the Lagrange multiplier vector. The eigenfrequency ($f_E$) is related to the eigenvalue by $f_E=-\lambda/2\pi i$.

$$ (\lambda_E - \lambda_0)^2 EU - (\lambda_E - \lambda_0)DU + KU + N\Lambda = 0 \quad (67) $$

Depending on the configuration being solved a fixed constraint or free boundary condition was applied to the edges of the substrate. A fixed constraint prevents the boundary moving in any direction. This simulates a glass substrate clamped at the endpoint. A 50mm by 10mm rectangular geometry with a thickness of 100µm was defined. For the solid mechanics physics module the only material properties required are the elastic modulus, the density and Poisson’s ratio. Fine meshing is not necessary for this model as there are no fine features to resolve. The relevant parameters for willow glass were taken from the glass data sheet. The FEM results indicate a resonance frequency of 223Hz in the glass substrate with fixed end conditions. This is in agreement with the analytical result which indicates a resonant frequency of 220Hz. The mode shape also matches with the predicted shape shown in Figure 6.2.

To study the stress caused by the displacement of the glass substrate a frequency domain solver must be applied. The eigenfrequency solver determines the resonant frequency and the mode shape of the system but the displacement is arbitrary and cannot be used to determine the stress. Using the frequency domain solver a harmonic perturbation can be applied to the substrate at the frequency determined in the eigenfrequency solver. The solver will calculate the response of the substrate to the applied load and the frequency at which it is applied. The amplitude of the oscillations is determined by the magnitude of the applied perturbation. The solution for the maximum displacement can be taken from the frequency domain solver and used in a stationary solver to determine the stress in the substrate. Figure 6.3 shows the solution for the stress tensor along the x axis for a harmonic perturbation at 223Hz with a magnitude of 0.9N. As expected the outer bending surface experiences a tensile stress while the inner bending surface experiences a compressive stress. The bending stress has
a maximum value in the centre of the substrate. The stress required to fracture a scribe in the glass was determined in section 5.5.2 and was 110MPa. The magnitude of the harmonic perturbation was increased until the displacement was large enough that the tensile stress in the central part of the substrate reached 110MPa. The corresponding displacement was 4.7mm.

Figure 6.3: Solution of FEM solid mechanics model for the stress in a displaced substrate with both ends fixed. Top and bottom views of the same substrate are shown. The displacement was determined from a frequency domain solver which perturbed the substrate at a frequency (223Hz) determined by an eigenfrequency solver. The substrate deformation and coloured contour lines indicate the displacement. The surface colour indicates the stress tensor along the x axis, and is positive for a tensile stress and negative for a compressive stress.

Figure 6.3 shows that the fixed ends of the substrate experience significant stress which is in fact higher than the stress in the central region. The outer edges experience a compressive stress while the inner edges experience a tensile stress. To ensure fracture only occurs along the scribed lines the outer edges must be free from any significant edge defects.

Figure 6.4 shows a line plot of variation of the calculated stress with substrate depth, measured at the central part of the substrate. The stress varies linearly from one surface to
another. There is a central layer which experiences no stress. This is an important feature as the depth of the stress raiser into the substrate should be less than this depth for it to experience significant tensile stress.

![Graph showing the variation of stress with substrate depth.](image)

**Figure 6.4:** Plot of the variation of stress with substrate depth. The measurement was taken at the central point of the substrate. A positive stress is tensile and a negative stress is compressive. A substrate depth of 0 indicates the outer bending surface and a depth of 100μm indicates the inner bending surface.

### 6.3 Experimental Method

The mechanical resonance setup outlined in section 3.3.9 was used to produce oscillations in a thin glass substrate. Scribed GLeaf borosilicate glass, with thickness of 100μm, was used in this test. The sample was held flat using two variable z stages. The edges were fixed to the stages using scotch tape, and held down with weighted metal blacks. Care was taken to tape as little of the glass as possible to minimise damping and reduction in vibrating length of the beam. A 24V square wave signal was used to control a high-speed solenoid valve. The valve controlled the output of a compressed air jet. The oscillations were recorded using the high speed camera setup described in section 3.4.5. The fracture was recorded from a side view allowing the oscillation amplitude to be determined. The camera was manually triggered.
6.4 Mechanical Resonance in Thin Glass

A 50x10mm GLleaf glass substrate was scribed along the centre of the short axis with a row of elliptical recesses produced using the technique described in chapter 5. The glass was scribed using a pulse energy of 180μJ and 250 pulses per spot (identical to the scribe shown in Figure 5.7 (a)). Using the analysis from section 6.2 this substrate has a natural vibrational frequency of 223Hz (FEM) and 220Hz (analytical) when fixed at both ends. Jets of compressed air at a pressure of 100kPa were applied periodically to the glass at a range of frequencies to determine the natural vibrational frequency of this configuration experimentally. The scribed surface was facing away from the air jet during tests. The signal generator did not allow variation of the duty cycle, which was fixed at 50%. Consequently at lower frequencies the air jet was switched on longer compared to higher frequencies. The maximum amplitude at each frequency was measured from the high speed recording of the oscillations (Figure 6.5). The recording was captured at a frame rate of 5.6kHz.

![Figure 6.5: A plot of experimental measurements of the frequency response of a fixed-fixed thin glass beam. The vertical displacement was determined from a still image taken from a high speed recording of the oscillation.](image)

The position of the centre part of the glass substrate was tracked using a Matlab script. The video was imported into Matlab and converted into a series of still images, each image representing a single frame in the video. The illuminated edge of the glass contrasted strongly against the dark image background. The position of the maximum pixel value from the centre
column of the image was determined, this corresponds to the position of the centre part of the substrate. A loop was run to calculate the position for every frame in the video (see appendix 8.1 for Matlab code used). Figure 6.6 shows plots of the sample displacement over time for four frequencies: 10Hz, 60Hz, 130Hz and 190Hz. The measurements were taken after the amplitude had settled at a constant value.

![Figure 6.6: Plots of the displacement of the centre of the glass substrate, which is perturbed by a periodic air jet, over time. The displacement was determined from the high speed recording using a Matlab script.](image)

### 6.5 Resonance Induced Fracture

To fracture the glass the substrate was driven by compressed air at the previously determined resonant frequency (130Hz). The pressure of the compressed air was increased to 140kPa using the pressure regulator to increase the oscillation amplitude. After 21 oscillations the amplitude had built up sufficiently to cause fracture of the substrate (Figure 6.7).
Figure 6.7: Stills from a high speed camera recording of a scribed glass substrate driven at its resonant frequency. The 6mm compressed air pipe is visible at the bottom of the images. The upper image shows the substrate immediately prior to fracture. The bottom image shows the substrate 0.54ms after fracture has occurred.

Figure 6.8 shows a scribed glass sample after fracture. The edge quality is good and identical to the results shown in section 5.5.2. This test was repeated on four other identical samples to verify the repeatability of the process. The number of oscillations which occurred before fracture varied from 17 to 32 with a mean of 24.8. The cut edge of each sample is consistent with Figure 6.8.
Figure 6.8: Microscope image of the edge of scribed glass sample after fracture using the mechanical resonance technique.

6.6 Discussion

The results of the frequency response test (Figure 6.5) on the thin glass substrate does not appear to indicate resonance occurring. However, the results of this test may be skewed due to the nonzero response time of the valve. The air pressure transmitted through the valve will increase slightly with time. The valve data sheet indicates the valve will take several milliseconds to open fully. Repeating the same test with a fixed pulse width would give a more accurate measurement of the frequency response.

Figure 6.6 shows the variation of the displacement of the glass substrate over time. For low frequency perturbations ‘ringing’ oscillations in the substrate are clearly visible after the valve has closed. The substrate oscillates at its resonant frequency until the remaining energy has been damped out of the system. If the glass substrate is being driven at its resonant frequency this will not occur. These oscillations have a frequency of 130.2Hz and give a strong indication of the resonant frequency of the system. Driving the system at 130Hz results in sinusoidal oscillations, further evidence that the system is oscillating at its resonant frequency. Driving the system at frequencies higher than its resonance frequency results in a reduced amplitude.
The predicted resonant frequency is 223Hz (FEM) and 220Hz (analytical) while the experimental data indicates a resonant frequency of approximately 130Hz. A reduction in the resonant frequency indicates damping in the system. The resonant frequency of a damped system will be shifted to lower values (see Figure 6.1).

Mechanical resonance can be used to fracture a scribed thin glass substrate. Air jets applied at the appropriate resonant frequency will cause oscillations in the substrate with increasing amplitude. At an air pressure of 140kPa, 21 oscillations were required before the amplitude was sufficient to fracture the glass along the scribe line (Figure 6.7). The time required to fracture the substrate is then 3.75ms. The edge quality after fracture is good (Figure 6.8).

### 6.7 Conclusions

A resonant vibrational mode was excited in a scribed glass substrate using a periodic perturbation which matched the vibration frequency of the fixed glass substrate. The bending of the beam produced a tensile stress on the upper bending surface. If the applied force is sufficient the bending stress will fracture the glass along the scribed path. The oscillation of the substrate was recorded using a high speed camera which showed the mode shape of the beam and allowed the frequency of oscillation to be determined. Precise determination of the resonant frequency is difficult as the duty cycle of signal generator is fixed and the high-speed valve appears to have a nonuniform response.

Two high speed valves, arranged equidistant to deliver air from above and below the substrate, could be used to achieve a more robust fracture process. If the valves are wired out of phase a push-pull arrangement could be affected. A higher amplitude could be achieved using this setup and the time required to fracture the substrate would be reduced.

A noncontact method for fracturing scribes produced in thin glass has been demonstrated. Combined with the mechanically inspired glass scribing technique discussed in chapter 5 this may form the basis of an effective glass processing technique for future reel-to-reel manufacturing platforms.
Chapter 7
Conclusions and Future Work

This chapter will summarise the primary accomplishments of the experimental study and discuss their significance in relation to the initial goals and the state of the art in literature. Future advancement of the experimental studies will be considered.

7.1 Full Body Laser Ablation

Full body laser ablation as a technique for glass processing is lacking. Performance in a number of key metrics, such as processing speed and cut quality, was modest. For CO$_2$ lasers thermal ablation is the dominant mechanism which is effective for vaporising the material. Large temperature gradients left in the unablated material lead to stability issues as the material cools and contracts. Short and ultrashort pulse lasers offer a more predictable full body ablation process but energy coupling and processing speeds are poor. A polarisation effect was identified chapter 4. Depending on the polarisation an increase in processing speed and a decrease in damage at the rear of the substrate was observed.

It is increasingly apparent that a singular laser process cannot meet performance targets. A hybrid HF etching processing to accompany full body ultrashort laser ablation was developed. The etching process slightly removes material from the rear surface while the laser ablates material at the front (see surface 4.4.4). A slight improvement in material removal efficiency was observed.

Alternative hybrid processing techniques are proposed below.

7.1.1 Laser Induced Plasma Assisted Ablation (LIPAA)

LIPAA is a processing technique for transparent materials where a laser pulse passes through the transparent substrate and strikes a metal target beneath. For fluences greater than the
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Ablation threshold of the metal target a plasma is produced which moves towards the rear side of the glass substrate. Interactions between the plasma and subsequent laser pulses causes ablation of the rear side of the glass substrate. The net effect is that we can ablate glass at fluences below the damage threshold. The ablation mechanism is a combination of three processes: influence of species in the plasma on the sample surface, plasma heating and thin-metal film deposition[160]. The dominant ablation mechanism is debated[160]. For ns pulse durations the laser induced plasma from the metal will reach the rear surface of the glass substrate during the duration of same laser pulse. The laser will interact with the plasma facilitating the transfer of charge and kinetic energy from the plasma ions to the material. High speed electrons in the plasma may also heat the material through the inverse bremsstrahlung mechanism. The plasma may deposit a thin metal film on the glass surface. The thin metal film will enhance the optical absorption in the material. Zhang et al demonstrated high aspect ratio hole drilling [161] and micrograting fabrication[160] in quartz using the LIPAA technique. Malhorta et al [162] improved on the feature quality in the LIPAA micromachining process. Ultrashort laser pulses were used to excite a plasma in water, and an external magnetic field was applied to manipulate the shape of the plasma and accurately ablate the target.

The potential for a hybrid LIPAA based thin glass cutting process has yet to be explored. A significant amount of the incident laser light is transmitted through the substrate when ablating glass with a short or ultrashort pulse laser. This energy could potentially be used in a LIPAA process to ablate the rear surface of the glass while the focused laser ablates the front surface.

7.1.2 Laser-Induced Doping and Ablation

Incorporation of electrically active dopants into silicon substrates using laser techniques has been well studied. Indium tin oxide (ITO) films are transparent conductive films coated on glass as part of touch screen display production. Being metallic in nature indium and tin atoms are highly absorbing of optical energy. By heating and melting regions of the ITO layer diffusion of indium and tin atoms into the glass could be promoted. Diffusion rates in the liquid phase is significantly higher than the solid phase due to enhanced transport by convection effects[42]. Heating could be achieved using a UV laser and a projection mask to selectively heat the areas which are to be cut. A high power short pulse laser can then be used to ablate the doped regions with higher efficiency, due to the increased absorption.
7.1.3 Rapid Variation of Focal Plane

Acoustically driven liquid lenses have been shown to enhance the depth of field, over standard optics for laser processing, by an order of magnitude [163]. Tight focusing conditions combined will allow for a narrow kerf with minimal edge chipping. Rapidly varying the focal plane will ensure the depth of focus is not an issue. The laser will be focused at the bottom of the kerf at all times. Ablating from the front surface followed by ablation from the rear surface may be a beneficial process.

7.2 Mechanically Inspired Scribing

The mechanically inspired scribing technique was developed as an alternative to ablative techniques for thin glass processing. The beneficial aspects of the mechanical scribing process were taken and adapted to a flexible and rapid laser process. Experimental results showed that glass processed with this method met the required standard for surface roughness and edge strength, although the edge strength is side dependent. Processing speed did not meet requirements however this is regulated by the laser source and scanning method used. Alternative high power high repetition rate lasers and galvo scanning methods will surpass desired processing speeds.

There are diverse opportunities for further development of this technique. There are near limitless numbers of possible optical designs, each with particular advantages and disadvantages. Some potential alternate designs are discussed below. The response of different materials to the laser stress raiser scribing is intriguing given the contrasting results for scribing of sapphire and borosilicate.

7.2.1 Curvilinear Scribing

Curvilinear shapes cut using the mechanically inspired technique showed some micrometer scale non-uniformities along the curved edges. The non-uniformities are due to the linear elliptical sections which approximate the curve. Uniformity can be improved by reducing the elliptical spot dimensions. Alternative optical designs are required to achieve this. One option is to use a singlet toroic lens to focus the beam to the desired spot dimensions. This will
eliminate the maximum power limitation inherent in the previous doublet design (Figure 5.2), however, the focused spot dimensions will be fixed.

A toroidal lens was designed using optical ray tracing software. A default plano-toroidal lens was used as a starting point for the design. A toroidal surface is defined by a curve in the YZ plane which is then rotated about an axis parallel to the Y axis but displaced by a distance \( R \); the radius of rotation. The curve in the YZ plane is given by (68). \( R_c \) is the radius of curvature, \( k_c \) is the conic parameter, \( y \) is the Y coordinate and \( \alpha_n \) is the coefficient on the power of \( y \) for the surface.

\[
z = \frac{R_c^{-1}y^2}{1 + \sqrt{1 - (1 + k_c)c^2y^2}} + \alpha_1 y^2 + \alpha_2 y^4 + \alpha_3 y^6 + \ldots
\] (68)

To optimise this design an arbitrarily selected radius of curvature was selected for the lens (30mm) and the other parameters left at zero. The lens thickness, focal length, radius of curvature, radius of rotation and \( \alpha \) parameters were set as variables. A boundary condition that the focal length of the lens must be at >100mm was imposed, as a large working distance is preferable. The optimisation procedure was run with a target of minimising the spot dimensions along the y axis. The optimiser produced an aspheric lens with a high radius of curvature and only a slight astigmatism. Figure 7.1 shows the optimised plano-toroidal singlet lens design. The lens thickness is 5.2mm. The radius of curvature is 56mm and the radius of rotation is 55mm. The alpha parameters are zero. The focused spot has dimensions approximately half of that achieved with the telescopic doublet design (Figure 5.2).
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Figure 7.1: Results of Zemax optical design. The main image shows the plano-toroic lens arrangement with the chief and marginal rays drawn. The light propagates through the system from left to right. The insert shows the focused spot dimensions after optimisation. The beam waist is 2.2mm prior to focusing.

This design has several advantages over the telescopical arrangement. The large working distance (100mm) reduces lens contamination issues. In the telescopical arrangement optical damage to the objective lens occurred for high powers. In this case optical damage to the objective lens will not occur as we have a single focusing element. The smaller spot result in an increased fluence incident on the glass. Consequently the laser dwell time per spot can be reduced. It may also be possible to use a higher pulse repetition rate to increase the processing speed.

An alternative solution to reduce the spot dimensions in the fixed lens setup is to introduce an additional optical elements into the design. Taking the telescopical design (Figure 5.2) we can add an additional spherical lens prior to the cylindrical objective lens. The lens separation and focal length are set as a variable. A boundary condition that the focal length must be at least 10mm was set. The optimiser was run to minimise spot dimensions along the y axis. Figure 7.2 shows the design with optimised lens separations. The spherical lenses are identical and have a thickness of 3.58mm and a focal length of 100mm. The cylindrical lens has a thickness of 5.22mm and a focal length of 100mm. The spot dimensions are reduced by approximately 50% from the doublet lens design (Figure 5.2). The advantage of this design is the use of in stock optical components reducing the cost of the design. There is also some flexibility in the spot dimensions as the separation of the lenses can be adjusted. Debris control
will be a challenging issue due to the short focal length. Increasing the boundary condition on the focal length in the design results in a large increase in the spot dimensions.

![Triplet lens arrangement with chief and marginal rays drawn. The design consists of two identical spherical lenses and a plano-cylindrical lens as the objective lens. The light propagates through the system from left to right. The insert shows the focused spot dimensions after optimisation. The beam waist is 2.2mm prior to focusing.](image)

**Figure 7.2: Results of Zemax optical design.** The main image shows the triplet lens arrangement with the chief and marginal rays drawn. The design consists of two identical spherical lenses and a plano-cylindrical lens as the objective lens. The light propagates through the system from left to right. The insert shows the focused spot dimensions after optimisation. The beam waist is 2.2mm prior to focusing.

Other optoelectronic components offer alternatives to optical elements for achieving the elliptical spot shape. A deformable mirror will allow for precise prefocusing of the laser prior to the objective lens. The spot dimensions would be fully adjustable and rotation of the elliptical shape could be controlled. A spatial light modulator could also be used to adjust the beam shape prior to focusing. This will enable alternative spot shapes as discussed in section 5.8.

The suggested designs in this section will reduce the non-uniformities and improve the speed and repeatability of the curvilinear scribing process.

### 7.2.2 Galvo Scanner Scribing

Developing an effective galvo scanning process to implement this scribing technique is key to delivering an industrially practical process. The focused spot dimensions are prohibitively large when scribing with the galvo scanner setup shown in Figure 5.3. The fluence is reduced by the spot dimensions and it is challenging to achieve consistent scribing. Optical design is
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complicated by insufficient information on the F theta lens dimensions, but it is clear a single
cylindrical lens cannot meet the required spot dimensions. To reduce the focused spot
dimensions an alternate optical design is required. Further details are required on the F theta
lens to progress this optical design.

7.2.3 Post Processing of Thin Glass

The uniformity of the edge was significantly improved by applying a thermal reflow process
(5.5.2). The amount of glass edge strength recovered by this process is an open question. The
reduction in edge defect size indicates an increase in the glass edge strength due to the reflow
process.

Other possible post processing procedures include sol gel coating and HF etching. A
sol gel coating applied along the cut edge which will fill in any non-uniformities. The sol gel
can then be cured in an oven where it will harden and bond with the glass. The solution
composition can be tailored to match the transparency of the bulk glass substrate. This may
offer another solution to improve the edge quality and strength of the processed glass. HF
etching was shown in section 4.4.4 to produce a smooth surface after etching (Ra=48nm). The
etching process could be applied to the cut edge to reduce any nonuniformities standing proud
of the surface and reduce surface roughness around the laser ablated feature.

7.2.4 Other Materials

The process is applicable to any brittle material, this includes glasses, ceramics and metals
cooled below the ductile-to-brittle transition temperature. The experimental results presented
in chapter 5 shows a considerable difference in the response of borosilicate glass and sapphire
to the scribing process. Microcracking was occurring in both cases however the cracking was
much more linear in the case of the sapphire. Consequently scribed sapphire is more suitable
for thermal fracture. Thermal fracture is preferable over mechanical fracture as it is faster,
repeatable and easily automated. The response of other materials is an open question.

Of particular interest is the response of materials with significant residual stress. Tempered glass has been shown to self-cleave after scribing due to the tensile stress layer in
the bulk of the material[98]. Producing an elliptical recess in the material with a depth sufficient
Conclusions and Future Work

to reach the tensile stress layer in a tempered glass sample may lead to self-cleaving. The depth of layer for gorilla glass (Corning) is 40μm. The residual tensile stress is 800MPa. The recesses shown in Figure 5.8 extend 22μm into the material. The recess depth is related to the number of pulses per spot. Increasing the number of pulses per spot may produce a recess with sufficient depth to reach the tensile stress layer. A self-cleaving step would reduce the complexity of the process, however it is only applicable to materials possessing residual tensile stress.

7.3 Resonance Cracking

A mechanical resonance technique was developed in order to cause stress and fracture in a scribed thin glass substrate. Periodic bursts of compressed air were used to oscillate a fixed glass substrate containing a scribe. By analysing high speed recordings of the oscillations the resonant frequency of the system can be determined. Applying periodic bursts of compressed air at this frequency will fracture the substrate, if the air pressure is sufficient. This technique has potential use in reel-to-reel manufacturing platforms for fracturing laser scribed thin glass substrates in a controlled manner.

7.3.1 Higher Harmonics

Exciting higher harmonic modes in glass gives rise to intricate mode shapes. This may be of use when fracturing densely packed features on the glass surface. Figure 7.3 shows the results of an FEM analysis on the mode shape of a thin glass beam oscillating at a high harmonic frequency. Localised deformation of the substrate is occurring. A large number of harmonics are available some of which oscillate with mode shapes with similar localised deformation. For fracturing non-uniformly spaced features the frequency could be swept between harmonics to stress different parts of the glass in a prescribed order.
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Figure 7.3: Solution of an FEM eigenfrequency analysis performed on a thin glass plate of dimensions 50x10x0.1mm. Both ends of the glass are fixed while every other edge is free. The solution shows the mode shape of the 15th harmonic. The surface colour and deformation indicate the displacement of the substrate. This harmonic mode has a resonant frequency of 6.47kHz. The displacement units in the plot are arbitrary. The simulations is an indication of the mode shape only.

7.3.2 Alternate Arrangements

Alternate clamping arrangements will allow more variation in the resonant mode shapes. A cantilever beam will oscillate at a lower frequency, and with significantly different mode shapes, than a beam with both ends fixed. Figure 7.4 shows a high harmonic mode shape in a thin glass substrate held in a cantilever arrangement. At the free end of the substrate we see nearly circular displacements occurring. This will cause a circular stress region in the glass. If the clamping is controlled in such a way that the circular displacement occurred on a circular scribed feature then tensile stress could be applied evenly to all sides of the shape. Alternate clamping arrangements combined with high harmonic perturbation may offer a solution to fracturing curved scribes in a single processing step.
Figure 7.4: Solution of an FEM eigenfrequency analysis performed on a thin glass plate of dimensions 50x10x0.1mm. All edges are free except the narrow edge at x=0 which is fixed. The solution shows the mode shape of the 15\textsuperscript{th} harmonic. The surface colour and deformation indicate the displacement of the substrate. This harmonic mode has a resonant frequency of 5.61kHz. The displacement units in the plot are arbitrary. The simulations is an indication of the mode shape only.

### 7.3.3 Resonance Process

The resonant frequency of the material was determined manually for the experimental work carried out in chapter 6. If the substrate is initially perturbed and left to vibrate it will settle into oscillations at its resonant frequency. A sensitive microphone could be used to record the compression waves produced by the oscillating glass substrate and determine the resonant frequency. The measured resonant frequency could then be used to automatically tune the driving frequency.

There are numerous alternative techniques which could be exploited to produce resonance in a substrate. These techniques include piezoelectric resonance and acoustic resonance, each with particular advantages and disadvantages.

A piezoelectric material will physically deform due to an applied voltage. Applying a varying voltage will produce a vibration in the piezoelectric material. The vibrational frequency varies with the frequency of the applied voltage. However, the crystal will have a natural vibrational frequency at which it easily oscillates which depends on the physical dimensions. Forcing the crystal to oscillate at frequencies other than its natural frequency will result in a decrease in oscillation amplitude. The variation in amplitude with frequency is given by equation (58). Bonding a piezoelectric disk to a glass substrate and applying a varying voltage to the disk will result in the vibrational frequency in the disk being transferred directly to the
glass. If the vibrational frequency of the disk matches the natural frequency of the glass substrate oscillations will build up. The oscillations will lead to stress which can be used to cause fracture along a weakened scribe line.

An acoustic speaker produces compression wave in air. A compression driver is a specialised type of acoustic speaker which uses an oscillating metal diaphragm to generate compressions and an acoustic horn to radiate the sound efficiently. The diaphragm is controlled by an electromagnet. A compression driver produces high sound pressures as the diaphragm area is typically twice as large as the throat aperture of the horn. This acoustic setup will produce ten times more sound power than a cone speaker transmitting an identical amplifier signal. Using a pair of compression drivers it may be possible to produce strong acoustic resonance in a glass substrate. Two drivers setup equidistant above and below a glass substrate, with one wired out of phase, will exert a push pull force on the substrate. If the frequency of the compression waves matches the natural frequency of the glass substrate oscillations will build up. The oscillations will lead to stress which can be used to cause fracture along a weakened scribe line. The size of the horn mouth required to effectively deliver sound waves becomes unfeasibly large at low frequencies. Consequently this technique is better suited to mid to high frequencies, 3.5-20kHz. This technique would be suited for exciting high harmonic modes and sweeping between different frequencies as discussed in sections 7.3.1 and 7.3.2.

7.4 Summary
Tangible progress has been in the study of laser scribing of thin glass with ultrashort laser pulses. An extensive parameter study was carried out which showed the impact of laser wavelength, pulse duration, applied laser fluence and scan speed on cut quality and ablation rate. A polarisation effect was identified and was shown to have a considerable influence on the quality of glass scribes produced using an ultrashort pulse laser. It was concluded that full body laser cuts cannot achieve sufficient speeds for an economical process. A controlled fracture technique was designed as an alternative. The cut quality and strength of this process was promising. A noncontact mechanical resonance fracture step was demonstrated to improve the suitability of the process for an industrial environment. The mechanically inspired laser scribing method has considerable potential for future development.
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Appendices

8.1 Matlab Code for Video Positon Tracking

The following code was used in section 6.4 to determine the displacement of the thin glass substrate from the high speed recording.

```matlab
%Script to Track amplitude of resonance oscillations

Vid = VideoReader('20Hz.avi');     %read in video
numFrames = get(Vid, 'NumberOfFrames')    %calculate number of frames
vidFrames = read(Vid);        %read information from each frame
Values=zeros(numFrames,1);    %create empty matrix to write values into

%loop to cycle through each frame and determine the position of the max value in the centre column of the image (column 400), which indicates the position of the centre part of the glass substrate.
for k=1:numFrames
    Frame = (rgb2gray(vidFrames(:,:,,:,k)));
    [I,Y]= max(Frame(1:400, 400));
    Values(k)=Y
end

%The position of the centre part of the glass substrate in each frame is now stored in the vector 'Values'.
```
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