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Pulsed Laser Material Interaction with Thin Indium Tin Oxide Films

Cormac McDonnell
A thesis submitted to the College of Science, 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
College of Science
National University of Ireland, Galway

Academic Supervisor:
Dr. Gerard O’Connor
Abstract

The interaction of short and ultrashort laser pulses with very thin films is currently an important area of research for laser material interactions. The interaction between the laser pulse and the thin transparent conductive film is key to the fabrication of touch panel sensors, light emitting devices, and photovoltaics. This thesis presents results obtained from an investigation of short and ultra-short pulses with very thin transparent conducting oxide films (TCOs). The experiments were all performed on indium tin oxide (ITO), which remains of critical importance to the many applications of TCOs in the industrial sector.

The selective patterning processes was characterised for nanosecond, picosecond and femtosecond laser pulses, using off-line techniques such as atomic force microscopy and real time plasma imaging. The results were analysed by the development of multi-physics simulations based on finite element modelling techniques. The film removal process was found to be dependent on laser wavelength, laser pulse duration, substrate material, and other beam delivery properties such as numerical aperture, laser spot radius, and laser shot number.

In nanosecond laser patterning, selective removal of the ITO film on glass substrates, for pulses with photon energies less than the ITO direct transition bandgap, is found to be non-ablative, principally driven by thermal melt flow. Pulses with photon energies greater than the bandgap result in ablation by vaporisation. The laser spot overlap is an important parameter for selective patterning; high shots per area result in film removal with smoother profiles and less glass damage. Also for nanosecond processing, the size of the laser spot was found to affect the threshold fluence; this is interpreted using an electronic localisation and diffusion model in the thesis.

In ultrashort laser patterning of ITO on glass substrates, the film removal process was found to be highly dependent on the applied laser fluence for picosecond and femtosecond laser pulses. The development and application of a two temperature simulation model, predicts that film ablation is principally driven by ultrafast lattice deformation. This is induced by the hot electron blast force, which leads to fracture of the ITO film at the film grain boundaries.
Film removal of ITO on flexible Polyethylene terephthalate (PET) polymer substrates, was found to be through thermo-elastic thin film delamination. The delamination process is found to be principally generated by the thermal expansion of the PET substrate during laser heating. This release mechanism was found to be independent of the wavelength and pulse duration studied. The selective patterning process is characterised by the ability to create a clean removal process using low numbers of shots per unit area.

Finally, the study examined the dependence of laser processing with a spatial beam profile using custom fabricated diffractive optics. A novel two-step fabrication method was used to generate high efficiency reflective diffractive optics. The spatially shaped, top-hat, laser beam profile was used to selectively remove the ITO thin film, which resulted in optimal processing, consisting of minimised re-solidified crater edges for nanosecond pulses.

In summary, the thesis provides a concise in-depth study highlighting the opportunities for selectively patterning highly degenerate semiconductors used as TCOs in current and future devices.
This thesis is based on a number of journal papers published in the following journals


Conference Posters:

“Effect of spot size and numerical aperture on the ablation threshold of ITO thin films” ERMS Strasbourg 2012

“Laser beam shaping and processing using reflective silicon Diffractive Optical Elements”

ERMS Strasbourg 2013
## Symbol List

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>( \phi_{th} )</td>
<td>Threshold fluence</td>
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<tr>
<td>( \phi_0 )</td>
<td>Peak fluence</td>
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<tr>
<td>( \omega_0 )</td>
<td>Laser spot radius</td>
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<td>( f )</td>
<td>Focal length</td>
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<td>( D )</td>
<td>Crater diameter</td>
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<tr>
<td>( I )</td>
<td>Laser intensity</td>
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<tr>
<td>( r )</td>
<td>Radial direction</td>
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<tr>
<td>( \lambda )</td>
<td>Laser wavelength</td>
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<td>( D_s )</td>
<td>Laser beam diameter</td>
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<tr>
<td>( z_r )</td>
<td>Rayleigh range</td>
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<td>( R )</td>
<td>Reflectance</td>
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<td>( \alpha )</td>
<td>Absorption coefficient</td>
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<tr>
<td>( d_\alpha )</td>
<td>Absorption Depth</td>
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<td>( n )</td>
<td>Electron density</td>
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<tr>
<td>( E_f )</td>
<td>Fermi level</td>
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<td>( m )</td>
<td>Electron mass</td>
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<tr>
<td>( E_p )</td>
<td>Laser pulse duration</td>
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<tr>
<td>( c_p )</td>
<td>Heat capacity</td>
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<td>( k )</td>
<td>Thermal conductivity</td>
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<tr>
<td>( T )</td>
<td>Temperature</td>
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<tr>
<td>( T_m )</td>
<td>Melting Temperature</td>
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<tr>
<td>( T_v )</td>
<td>Vaporisation temperature</td>
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<tr>
<td>( \rho )</td>
<td>Density</td>
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<tr>
<td>( Q )</td>
<td>Laser source</td>
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<tr>
<td>( p_r )</td>
<td>Recoil pressure</td>
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<tr>
<td>( R_g )</td>
<td>Gas constant</td>
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<tr>
<td>( j_i )</td>
<td>Atomic flux</td>
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<tr>
<td>( k_B )</td>
<td>Boltzmanns constant</td>
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<tr>
<td>( T_e )</td>
<td>Electron temperature</td>
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<tr>
<td>( T_l )</td>
<td>Lattice temperature</td>
</tr>
<tr>
<td>( C_e )</td>
<td>Electron heat capacity</td>
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</table>
Lattice heat capacity $C_l$
Electron thermal conductivity $k_e$
Electron phonon coupling constant $G$
Fermi temperature $T_F$
Fermi velocity $v_F$
Speed of sound $C_s$
Keldysh parameter $\gamma$
Band gap $E_g$
Heat diffusion length $l_t$
Plasma front position $R$
Material strain $\varepsilon$
Material stress $\sigma$
Material expansion coefficient $\alpha_T$
Ripple periodicity $\Lambda$
Incubation parameter $S$
Laser Pulse Number $N$
Laser pulse energy $E_p$
Laser repetition rate $Q_l$
Laser power $P$
Thin film thickness $d$
Plasma frequency $\omega_p$
Imaginary refractive index $n_i$
Relative permittivity $\varepsilon_0$
Electron Flux $J_n$
Electron Diffusivity $D_n$
Electron Diffusion Coefficient $D_n^\alpha$
Surface Tension $\gamma$
Acknowledgments

There has been a lot of people over the course of these past 5 years who have contributed to the making of this thesis, some in an academic sense, but many more people who have helped me get through all the good, and not so good times that a PhD can bring.

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Finally, I would like to dedicate this thesis to my late mother Marie Costello, who I still miss every day.
“If it’s one thing I know,
it's that I know nothing,
and I am not even sure I know that”

Socrates
The work in this thesis is based on research carried out at the National Centre for Laser Applications (NCLA), School of Physics, National University of Ireland Galway. I, Cormac McDonnell 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

1. Introduction

The discovery and development of the Laser (Light Amplified Stimulated Emission of Radiation), has driven countless applications in fields such as material processing, material characterisation, telecommunications, medicine and large scale modern applications, such as potential nuclear fusion devices. This demand from industrial sectors for new and innovative laser applications, highlights the importance in understanding the physics behind these applications. As laser technology rapidly advanced from its initial beginnings, increasing in both technical specifications and decreasing in cost, the industrial sector has embraced laser technology for the development of processes in many areas, such as material drilling, welding, soldering and cutting. Another area which has seen significant industrial interest is the application of lasers to pattern display and touchpanel devices. These consist of thin films (< 100 nm) of transparent conducting oxides, deposited on glass or polymer substrates. Sensitive laser processing has been shown to outperform traditional lithographic processes in certain areas such as etch speed and pattern configurability. This allows the development of roll to roll processing, with faster throughput times and a more environmentally friendly process. The rapid advance in thin film technology has led to significant improvements in display device technology, specifically enabling the development of the capacitive touchscreen sensor, which are a vital component in modern display devices. The capacitive touchscreen acts a position sensing circuit. When the user touches the screen, a capacitive charge is set up between the front glass panel and TCO. In order to read the finger position, electrodes must be etched into the TCO, typically in a grid or diamond pattern.

Indium Tin Oxide (ITO) is the main thin film TCO in the display device sector due to its high conductivity, high transparency and high quality of thin film deposition. A number of other novel materials are currently being researched with the view of replacing ITO, including graphene, silver nanowires, Zinc Oxide (ZnO). While these materials offer good optical properties in a number of areas, there is a number of disadvantaged which
are holding back their introduction to large scale industrial processing. Laser processing to selectively pattern transparent conducting oxides has a number of advantages over traditional lithography processes, allowing the development of clean, re-configurable large area processing. However, creating stable and efficient laser processing shows many challenges. Selective removal of the film with no damage to the glass substrate and minimal ridge height at the laser scribe edge, is the optimal desired process features for display devices. These factors reduce the laser line visibility and improve the device yield rate. As industry moves towards thinner films and substrates, the challenge for damage-free selective ablation increases.

Currently, patterning of touchpanel TCO display devices in industry is carried out primarily using laser ablation processes and lithography. Both processes have their advantages. For lithography, accurate patterning with minimal substrate and excellent edge quality make it attractive for thin film applications. However, it requires multiple masks and chemicals, resulting in a process which is not suitable for high speed roll to roll processing. The goal of using lasers for this type of processing is to deliver a reliable, large area, and high throughput machining processes. However, there is a number of challenges which can lead to sub-optimal laser processes. Beam delivery to the sample is controlled using a direct write process, which uses galvanometer mirrors and lens control system to write the information in to the material. The spatial resolution of the process is dependent on the laser spot size and resolution of the positioning system. In terms of machine setup, a number of factors are important in the industrial setting, including the choice of laser wavelength, laser pulse duration, and the cost effectiveness of each process. These parameters will have a large impact on a number of factors including material throughput, process quality, cost of ownership, process control ability and reliability. Therefore, a thorough understanding of the laser material ablation process is an important research topic.
This thesis gives an account of laser ablation of thin TCO films, specifically Indium Tin Oxide (ITO), on glass and Polyethylene terephthalate (PET) substrates, along with the development of processes for selective removal of the film, taking into account parameters such as wavelength, pulse duration and the development of a beam shaping method using diffractive optics. The lasers used in this study have pulse durations in the nanosecond, picosecond and femtosecond time regime. The aim of the work is to increase the understanding of the interaction and ablation of laser pulses between the thin film and substrate. This was achieved using in-depth surface characterisation, ablation imaging techniques, and finite element thermal simulations. Laser ablation experiments were carried out investigating the effect of various laser parameters on the surface topography of the films. The results were compared to a finite element thermal model developed to show the temperature profiles in the film and substrate. Real time plasma imaging was used to visualise the laser ablation process. Comparison of the results provides insights into the mechanism for ablation of the film and substrate.

1.1. Objectives

The main objective of this work can be summarised as follows

1. To identify the film removal methods of very thin ITO films from glass and polymer substrates. This was achieved using a combination of experimental and computational techniques. The impact of this is to provide a full understanding
of the film removal mechanisms for ITO on glass and PET, and its dependence on key parameters such as laser wavelength and pulse duration.

2. To examine the effect of parameters associated with pulsed lasers on the ablation of the thin film, such as laser spot overlap, laser spatial beam profile and laser pulse number.

1.2. Chapter Synopsis

A literature review is given discussing the extensive research into laser ablation in Chapter 2. The mechanisms of laser energy deposition in materials are discussed for a range of bulk and thin film materials such as TCO’s, dielectrics and polymers. Diffractive optics are also considered, looking at the various fabrication and development methods and their implementation in laser material processing.

An overview of the experimental techniques is presented in Chapter 3. This provides a summary of the laser systems used, ranging from nanosecond to femtosecond pulse durations. The optical delivery of the laser pulses to the sample is also described. The surface characterisation methods and their implementation are detailed. A full description of the plasma imaging using iCCD photography is given, along with the methods used to generate the variable delays necessary to achieve the temporal precision required by the technique. The formulation of the computational simulation methods are shown. The finite element methods are discussed, along with material parameters, mesh development and various assumptions used in the simulations.

Chapter 4 describes the experimental results across the range of laser sources used. Firstly, nanosecond laser ablation of ITO on dielectric glass substrates and plastic PET substrates is reported. The surface topography of the nanosecond laser crater was examined in terms of selective removal of the film, along with analysis of crater edge and crater floor. The effect of parameters such as laser spot radius and numerical aperture on the applied threshold fluence is also investigated. Picosecond and femtosecond ablation results of ITO deposited on glass and PET are discussed in terms of the selective removal of the film from the substrate. Plasma imaging was used for nanosecond and femtosecond pulse durations, in order to show the expansion of the plasma on a nanosecond time scale. Ablation of ITO films on polymer PET substrates is examined, in terms of threshold fluence and surface morphology. Real time plasma imaging is used to visualise the
expanding laser plasma in the nanosecond time regime. Other issues are examined such as laser pulse overlaps, laser pulse incubation, rear-side laser illumination, and the effect of increasing film thickness. The development the diffractive optical elements (DOE’s) for spatial beam shaping is also described. The overall development is divided into a number of steps. Firstly, the phase profile to be implanted on the material is optimised using Fast Fourier Transform (FFT) methods. The phase profile is then realised on the silicon wafer using a two-step fabrication method consisting of a Focussed Ion Beam (FIB) implantation and a Reactive Ion Etch (RIE). Optical characterisation of the diffractive optics using nanosecond laser sources is described along with their application for patterning of thin film materials such as ITO on glass.

In Chapter 5, the interaction of the laser pulses and the thin film is examined using computational finite element simulations. The finite element thermal model is introduced and is used to model the experimental results, giving new insights into the ablation mechanism. In order to examine the temperature profile in the film and substrate for ultrashort pulses, a two temperature model (TTM) of the electronic and lattice subsystems was developed. The TTM was further expanded to show the effect of ultrafast lattice deformation, due to the rapid increase in the electron temperature during ultrashort laser pulse absorption. In the case of ITO on PET, a thermal stress model was developed to show the effect of thermal expansion at the film substrate interface. In the case of the ultrashort pulse interaction with ITO, the two temperature model was integrated with the thermal stress model, to provide an insight into the stress development during irradiation with ultrashort pulses.

In Chapter 6, the experimental and computational results are discussed, and the mechanisms for the ablation of the thin film are proposed. Selective removal of the film for ITO on glass is shown to be through thermal melt flow using nanosecond laser pulses. As the pulse duration is decreased into the ultrafast time regime, the primary method of thin film removal is by ultrafast lattice deformation by the hot electron blast force, leading to break up of the film at the grain boundaries. Film removal for ITO on polymer PET is shown to be through film de-lamination, due to thermal stress at the film substrate interface, generated by thermal expansion of the polymer substrate.

Finally, in Chapter 7, an overview is given of the thesis and the overall impact is discussed in terms of thin film ablation. Future potential work in this area is also discussed.
Chapter 2

2. Literature Review

In this section a wide range of the current laser ablation and laser material interaction topics are reviewed. The background for the interaction of lasers with thin films is reviewed, in order to gain a sufficient understanding of the both material and laser properties used in this study. Firstly, the materials used in this study are introduced, taking into account their optical, electrical and mechanical properties. The generation of laser pulses with nanosecond and ultrashort pulse durations is shown, along with the important laser output optical properties. The interaction of the laser pulse with materials is discussed for a variety of laser properties. Nanosecond pulsed laser absorption is compared to ultrashort pulsed laser processes, in the context of both bulk and thin film ablation. The absorption mechanisms of the material are shown using the Fourier heat equation for long nanosecond pulses, and the TTM model for ultrashort laser pulses. Relevant ablation mechanisms are discussed, taking into account the changes observed for different materials and pulse durations. The ejection of laser plasma and material removal via the ejection of the plume is also shown, along with the relevant models used to describe the plasma expansion. Beamshaping techniques, specifically diffractive optics, are reviewed in terms of laser machining of materials.
2.1. Materials

2.1.1. Indium Tin Oxide

The application of materials for use as a TCO requires a number of key material properties. The material must have a high transparency in the visible wavelength range, high free carrier density, low resistivity, high conductivity, high rate large area deposition and high mechanical adhesive strength. These properties are generally realised by taking semiconductor oxides which typically have a large bandgap, and doing them with rare earth metals, such as Al doped ZnO (AZO) and Sn doped In$_2$O$_3$ (ITO). The current most widely used TCO is ITO, and is currently used in many applications such as transparent electrodes in display devices [1], photovoltaics [2], low emissivity windows [3], light emitting diodes [4] and transparent thin film transistors [5]. However, due to the scarcity and high price of In, current research is underway to find a replacement for ITO films, with research focusing into graphene [6] and silver nanowires [7].

ITO films have a very low resistivity, due to its high free carrier density of electrons [8]. This gives a Fermi level which is situated at the bottom of the conduction band. The band gap of the material is approximately 3.6-3.8 eV [9]. The large density of free electrons is generated during the fabrication process by doping with Sn atoms. The crystal structure of the ITO is dependent on the fabrication conditions, and also the % of Sn doped in the sample. The crystal structure of indium oxide is bixbyite crystal structure, with 16 In$_2$O$_3$ molecules in the unit cell [10]. The Sn substitutional dopant replaces In, donating free electrons which increase the conductivity [11]. Increasing the % doping of Sn effectively increases the bandgap, as the conduction band becomes partially filled after doping. The bandstructure of ITO has been studied using ab initio methods, such as the linear muffin tin orbital method (FLMTO) [12]. The band gap is established by the Burstein shift, which compensates for the lowering of the band gap due to the many body effect. A highly dispersed and single character s-band is visible at the bottom of the conduction band. The doping also opens an additional bandgap, due to hybridization of Sn and In s states. The high density of electrons leads to wide absorption across a range of wavelengths. Typical absorption spectrum show the highest absorption in the deep UV and UV. The visible spectrum shows the lowest material absorption, with absorption increasing again in the IR. Ideally for TCO’s the visible region should be 100 % transparent, however in general
transmission ranges from 90-95 % for fabricated ITO films. The optical and electrical properties of the film are highly dependent on the electronic density, and also the grain size of the film. Variations in fabrication conditions [13] and film thickness [14] lead to varying values for the electron density, band gap and transparency. The electron mobility in the film is quite low, this is mainly due to scattering and absorption with impurities such as oxygen vacancies and at grain boundaries, with a value typically in the region of 15-40 $cm^2/Vs$ [15]. The structure of the film can also change from polycrystalline to amorphous depending on the fabrication conditions, and also the substrate material [16]. Fabrication of ITO films is primarily through DC magnetron sputtering [17], RF sputtering [18] and pulsed laser deposition [19]. Magnetron sputtering is the main process for deposition of ITO films on glass substrates. The sputtering process is common for obtaining films with a homogenous distribution and low surface roughness. In the sputtering process, gas ions out of a plasma are accelerated towards a target. In magnetron sputtering, a ring magnet is placed below the target, this is done to increase the ionization through secondary electrons, which become trapped above the target by the magnetic field. DC magnetron sputtering is restricted to material which are conducting, like semiconductors and metals. RF sputtering uses an AC voltage applied to the target. In the production of ITO films, $In_2O_3$ and $SnO_2$ targets are prepared from powder form. Large amounts of research have been done as regards depositing ITO films on glass and PET substrates. Extensive studies on the effect of parameters such as ITO target composition [20], Sn percentage [21], oxygen and hydrogen partial pressure [22], annealing temperature [23] and substrate temperature [24] have been undertaken.

2.1.2. Glass

The application of glass as TCO substrate for touchpanel development has been used for a long period of time, due to its high transmittance and acceptable mechanical strength [25]. Traditionally, deposition of TCO’s is typically carried out on soda lime glass or one of its variants. [26-29]. Soda lime glass is manufactured from a range of raw materials which are fabricated in a furnace, typically consisting of Sand ($SiO_2$), Soda Ash ($Na_2CO_3$) and Limestone ($CaCO_3$) amongst others. However, the next generation of TCO’s are deposited on chemically strengthened “Gorilla Glass” [30], which provides superior mechanical strength to soda lime glass.
2.1.3. Polymers

The application of polymers for use as substrates for the development of ultra-thin flexible display devices has recently been under consideration in the literature [31-35]. Ultra-thin polymers are a good candidate for TCO deposition due to their high transmittance in the visible wavelength region [36] and good mechanical durability [37]. The general structure of all polymers consists of repeating structural units called monomers. Covalent bonds hold the molecules together, with secondary bonds holding the polymer chains together. The exact polymer structure can contain numerous different molecule additions, resulting in many different polymers with varying optical and mechanical properties such as polyethylene terephthalate (PET) [38], Polyether ether ketone (PEEK) [39], para-methoxy-N-methylamphetamine (PMMA) [40] and Polyimide (PI) [41]. Figure 2.1 shows the typical PET monomer structure.

![Figure 2.1 PET monomer structure. PET monomers are cross linked with other monomers via hydrogen bonds](image)

The thermal and mechanical properties of PET are much different than the TCO’s deposited onto the polymer substrate. Typically PET has a large coefficient of thermal expansion and a large Young’s Modulus.

2.2. Laser beam propagation

Lasers used in material processing emit at specific wavelengths, typically from the ultra-violet (UV) to the Intra-red (IR). The most common lasers in the nanosecond pulsed time regime are generated by Diode Pumped Solid State (DPSS) lasers at 1064, 532, 533 and 266 nm. The shorter wavelengths are generated by high harmonic generation. Due to the laser cavity setup of these lasers, the fundamental transverse spatial output is Gaussian.
The laser beam intensity $I(r) \ (W/m^3)$, centred at $r = 0$ in $TEM_{00}$ mode is given by [42]

$$I(r) = I_0 \exp \left( \frac{-r^2}{\omega_0^2} \right)$$  \hspace{1cm} (1)

where $r$ is the radial co-ordinate and $\omega_0$ is the $1/e^2$ radius. The laser pulse emitted from the cavity diverges slightly, as the laser pulse exits the aperture. This property is described by the $M^2$ divergence factor. The $M^2$ factor describes the quality of the laser beam; it is given by the ratio of the beam parameter product of a real beam to an ideal Gaussian beam. The beam parameter product is given as the product of the beam radius and the divergence half angle. An $M^2$ factor of 1 gives a diffraction limited beam, with increasing $M^2$ values indicating reducing laser beam quality. The typical setup for delivering laser pulses to the material is a laser direct write configuration [43]. In this case, the collimated laser output is expanded to fill the appropriate aperture, and directed into a galvanometer scanning mirror system with a telecentric lens. The galvanometer consists of two movable mirrors, which can be used in conjunction with software, to control the position and movement of the laser beam on the lens. The telecentric lens itself typically consists of a series of compound lenses. It delivers the laser beam so that it is orthogonal to the surface at the focal plane. The optimised lens results in a minimal variation on the focal position across the field range. The transmitted laser beam is focussed at a position beyond the lens at its working distance $f$. The working distance is approximately the effective focal length of the lens assembly. The spot radius at the laser focus is approximately given by

$$\omega_0 = \frac{2fM^2\lambda}{\pi D_s}$$  \hspace{1cm} (2)

where $f$ is the focal length, $\lambda$ is the wavelength and $D_s$ is the laser beam diameter at the lens. The spot radius at any point after the focal point $\omega(z)$, can be determined from Gaussian beam propagation theory as

$$\omega(z) = \omega_0 \left[ 1 + \left( \frac{M^2 z}{z_r} \right)^2 \right]^{1/2}$$  \hspace{1cm} (3)
where \( z \) is the distance from the focal point and \( z_r \) is the Rayleigh range given by \( z_r = \frac{1}{\omega_0} \) \( NA \), where the numerical aperture (NA) is given by \( NA = \frac{f}{2D_s} \) if \( z \gg z_r \), or if \( z \leq z_r \), then the Rayleigh range is given by \( z_r = \frac{\pi \omega_0^2}{\lambda} \). Figure 2.2 shows how the spot radius propagates for a Gaussian pulse with a normalised spot radius = 1, with a normalised Rayleigh range = 1.

\[
\begin{align*}
\text{Normalised spot radius} & \quad \text{Normalised de-focus} \\
1.45 & \quad 0.0 \\
1.40 & \quad 0.1 \\
1.35 & \quad 0.2 \\
1.30 & \quad 0.3 \\
1.25 & \quad 0.4 \\
1.20 & \quad 0.5 \\
1.15 & \quad 0.6 \\
1.10 & \quad 0.7 \\
1.05 & \quad 0.8 \\
1.00 & \quad 0.9 \\
\end{align*}
\]

Figure 2.2 Laser spot radius propagation for laser focus with normalised radius = 1, and a normalised Rayleigh range = 1

### 2.3. Laser Beam Shaping

When delivering energy to a material, the Gaussian spatial beam shape is not always the most efficient method. The non-uniform energy distribution can lead to substrate damage by excessive ablation at the beam centre compared to the edge tip [44]. When overlapping spots are used to create an ablated line, the Gaussian distribution can lead to uneven trench morphologies [45]. Laser beamshaping involves the process of changing the spatial intensity of a laser pulse to another spatial profile, often a tophat distribution. A number of methods can be used to achieve the desired spatial profile, most of which have their own inherent advantages and disadvantages.
2.3.1. Mask Imaging

One of the simplest methods of changing a Gaussian spatial distribution to a tophat spatial distribution is mask imaging. Mask imaging has been used with femtosecond laser systems [46], with spatial beam resolution of 13 µm. Fringes due to diffraction were observed at the edge of the ablated pattern. This diffractive pattern can be a problem for high powered laser systems with appreciable coherent lengths, where the undesired higher diffractive orders can be patterned in a material. Mask systems are most often used in excimer laser systems of low coherence length, examples include the ablation of thin films [47], and 150 nm ITO on PET films [48]. While mask imaging can provide a tophat good with a consistent spatial intensity, the optical setup has a number of other disadvantages. Large energy losses are inherent in this type of system, typically the efficiency of the system is ≈ 10 %, as the mask must typically be much smaller than laser beam, in order to achieve the necessary level of tophat intensity. Achieving small feature sizes can also be difficult. This is due to the conditions necessary for ablation at the image plane. The de-magnification achieved at the image plane is directly related to the distance from the mask to lens. Typically, in order to achieve a good de-magnification, distances of over 1m between the mask and the final focusing lens are required. However mask imaging provides a low cost and configurable solution to beam shaping.

2.3.2. Refractive Shapers

Refractive optics are another popular current method of beamshaping [49]. In this method, the spatial intensity of the laser beam is changed through the use of a multiple lens system. Refractive shapers use the method of field mapping. These lens systems are commercially available, with companies selling refractive shapers, designed specifically for certain laser wavelength bands. The use of refractive shapers with high power lasers systems has been demonstrated experimentally [50].

2.3.3. Spatial Light Modulators

Spatial light modulators (SLM) are a re-configurable method for laser beamshaping [51]. SLM’s modulate the intensity or phase of the incident laser beam. SLM’s use liquid crystal materials to modulate the incident laser beam. Typically cells in the liquid crystal
are electrically addressed; the applied electric field modifies the optical properties of the liquid crystal. SLM’s can be transmissive (LCD) or reflective (LCOS). The desired spatial profile of the laser pulse is achieved through imparting a phase difference on the incident pulse, which causes a redefinition of the intensity profile. Spatial and temporal shaping of laser pulses using SLM technology has been extensively reported in the literature. SLM’s have shown good results for parallel processing, where the incident laser pulse is separated into an array of multiple parallel laser spots. This has been demonstrated using both femtosecond [52] and nanosecond [53] laser pulses. The use of SLM’s has also been demonstrated in the generation of non-standard laser beam profiles, which often have interesting characteristics, such as Bessel beams [54], and radial and azimuthal polarised beams [55].

2.3.4. Diffractive Optical Elements (DOE)

Diffractive optics are a popular method for beamshaping. DOE’s are well known for their ability to perform complex modulations of the phase and amplitude of light waves, not possible using refractive elements. The basic principle behind the operation of a DOE, is the imparting of a desired phase shift onto part of the incoming light wave relative to other parts of the same beam. The simplest way to describe DOE operation is in terms of a Fourier transform

\[ P(x, y, z) = FT[p(x, y, 0)e^{i\phi}] \]  \hspace{1cm} (4)

where \( P(x, y, z) \) is the diffracted field, \( p(x, y, 0) \) is the field at DOE surface, and \( e^{i\phi} \) is the DOE phase profile. This phase shift can calculated using a number of methods, using scalar theory, electromagnetic analysis and computer generated holography [56].

2.3.5. Computer generated holography (CGH)

The simplest type of diffractive element to gain widespread use was the Fresnel zone plate, later becoming the Fresnel lens [57]. The surface structures for these elements can be derived using Fermat’s principle, and are shown to give a theoretical efficiency of 100%. The phase profile of Fresnel lens DOEs can be solved analytically, however for
many more complicated DOE’s, no analytical solution exist, so algorithms are used to approximate the phase profile. In the literature there many papers which deal with the optimization of the phase profile using different techniques such as Fast Fourier transforms (FFT), which are known as iterative algorithms. Along with simulated annealing and genetic search algorithms which are non-iterative.

The most widely used algorithm is the Inverse Fourier Transform Algorithm (IFTA) [58]. This algorithm used an FFT method for phase retrieval, commonly referred to as the Gechberg-Saxton algorithm.

Another method of computing the phase profile is to use a hybrid algorithm approach, combing the iterative IFTA with a non-iterative algorithm [59]. The results showed that a hybrid approach may give better results than an IFTA approach on its own. However the results were not compared in terms of efficiencies, signal-noise or in a real beam shaping application. Another technique involves using a genetic algorithm combined with a gradient search technique [60]. This study used two real beam shaping applications, the conversion of a Gaussian to flat-top beam and Bessel beam. Very low signal-noise ratios were obtained with high efficiencies of over 95%. High efficiencies and low signal–noise ratio were also obtained using a modified IFTA approach [61]. The algorithm consisted of an initial IFTA approach until a stable solution was found, then modified constraining functions were added in the Fourier domain. Overall, many techniques can be used for generation of the DOE phase profile. Theoretical efficiencies up to 97 % can be obtained for complex phase designs.

2.3.6. DOE fabrication

The calculated phase profile must then be imparted onto an optic material, which can be either transmissive or reflective. Many methods have been studied, which can be used to imprint the phase profile into the material. The fabrication of DOE’s can be spilt into two types, methods that can fabricate a smooth kinoform profile, and methods which generate multilevel step profiles. The large majority of fabrication methods are only capable of multilevel DOE fabrication.

One of original methods for fabrication of diffractive optics is diamond point turning [62]. Using a shaped diamond turning point, kinoform profiles can be fabricated. This method allows the quick fabrication of elements. More complex structures are not feasible using
this method. Fabrication of a kinoform can also be done using other methods such as combined focused ion beam and reactive ion etch process [63]. Kinoform continuous profiles can be achieved using this method, which is only a two-step manufacturing process. High diffraction efficiencies of over 90% have been achieved using this method.

Most fabrication methods are multi-step. These methods use a series of masks and etch steps to create the profile. These methods range from e-beam/ion etch [64], DMD photolithography [65], grey-scale photolithography [66] and direct laser writing [67].

The efficiencies of the DOE’s are mainly dependent on the ability of the fabrication method to re-produce the desired phase profile. The effect of multi-step processes was examined [68]. In a multi-step fabrication process each individual step in the process, often adds additional errors due to mis-alignment at each step. It is clear from the literature that each fabrication method has its own advantages and dis-advantages, with fabrication process being the main cause of the reduction in the efficiency of the designed DOE.

2.3.7. DOE processing of materials

The use of diffractive optics for material processing has been studied for a limited number of materials. The use of diffractive optics for multi-beam parallel processing of crystalline solar cells was investigated using ultrashort pulses [69]. Overall, the ablation efficiency was increased by a factor of three, resulting in a > 50 increase in throughput speed. A tophat DOE was used in conjunction with nanosecond and ultrashort laser pulses, for drilling and laser marking of metal films, drilling of a silicon wafer, and laser marking of a solar cell [70]. Improvements on the laser scribe uniformity were seen. Overall, the application of top-hat laser pulses for material removal is still under-researched in the literature.

2.4. Laser energy absorption in the nanosecond pulse regime

A short discussion on the absorption of light by materials using nanosecond pulsed lasers is presented. Key parameters for thin films such as the material absorption coefficient and the Fourier heat equation are discussed. The effect of different materials electron bandstructure is shown in terms of the impact on the absorption of nanosecond laser pulses.
2.4.1. Fresnel Absorption

As the laser is incident on a material, three main processes take place as the light crosses the air material interface. According to Fresnel's law, a certain fraction of the light will be reflected at the material air interface, at normal incidence, this is given as $R(\lambda)$. This parameter is dependent on the refractive index change between the two media, given at normal incidence as

$$ R = \frac{(n_1(\lambda) - n_2(\lambda))^2}{(n_1(\lambda) + n_2(\lambda))^2} $$

(5)

Where $n_1$ and $n_2$ are the refractive index of the respective media. The remaining laser pulse energy is then transmitted and absorbed through the material, depending on the complex part of the material refractive index. The simplest description of laser absorption is given using the Beer Lambert law, where the laser intensity is attenuated exponentially into the material [71], given by

$$ I(z) = (1 - R(\lambda))I(0)\exp[\alpha(\lambda)y] $$

(6)

This equation describes the exponential decrease in laser intensity as the pulse is transmitted through the material, where $\alpha(\lambda)$ is the material absorption coefficient, $I(0)$ is the incident light intensity and $I(z)$ is the light intensity at a depth $y$ into the material. Large values of $\alpha$ lead to greater optical absorption and heating in a smaller depth. The optical penetration depth is given as $1/\alpha$. The absorption properties of the material are dependent on how the incident laser photon with the electronic structure of the material, and how the subsequent interaction of the excited electron takes place with the lattice. This means the laser absorption properties are highly dependent on the incident wavelength of the laser, along with the material optical and electronic properties of the material.
2.4.2. Material Bandstructure

Absorption of the incident laser photon by the material take place in two steps. First absorption takes place via the electronic subsystem, before the energy is transferred to the atomic lattice [72]. As electrons of the individual atoms are brought together in a solid, the quantised energy levels of the electronic system spread out into bands of allowed energy states. The allowed electronic wave functions from periodic plane waves. Plots of the bandstructure show the energy of the electrons as a function of the crystal momentum $k$, in the reciprocal lattice. The bandstructure itself is dependent on the atomic bonding and structure of the material, and can be split into three general cases, constituting metals, semiconductors, and insulators, all of which are relevant to this project.

2.4.3. Laser Absorption in Semiconductors

The crystal structure of semiconductors leads to an electronic structure which consists of a lower valence band, and an upper conduction band. These two bands are separated by an energy gap $E_g$, which is typically in the range of a few eV’s. Electrons can transfer between bands if the incident photon energy is high enough to excite the electron across the band gap, and the selection rules of the valence and conduction electrons overlap. In metals, the Fermi level $E_f$, lies in the conduction band and intraband electronic transitions dominate the absorption process. A band gap exists between the valence and conduction band for semiconductors, with the Fermi level located in the gap, its precise location depends on the doping level in the material. If the incoming photon energy is high enough, an electron at the top of the valence band will be promoted to the conduction band. The semiconductor bandstructure also support of free carrier transitions. This occurs when the energy of the incident optical photon approaches the band gap energy inter-band transitions can occur. In this case, an electron absorbs the incident photon and is excited to a higher energy level, leaving behind a vacant hole in the valence band. These transitions can either be direct, where crystal momentum is conserved ($\Delta k = k_c = k_v$). They can also be in-direct, where emission or absorption of a phonon is required. For direct transitions, the form of the absorption coefficient goes as $\alpha(\omega) \sim (\hbar \omega - E_g)^{1/2}/(\hbar \omega)$. The bandgap is also known to have a temperature dependence, which may have an importance for nanosecond laser interactions, where the
later part of the pulse interacts with a heated lattice. In general, the band gap energy decreases with increasing lattice temperature [73].

The electronic properties of semiconductors can be altered by n-type or p-type doping, resulting in a shift of the Fermi energy. As the doping level is increased, the bandgap edges are distorted at the valence band or the conduction band. For n –type doping, this results in an increase in electrons populating states within the conduction band; hence this pushes the Fermi level to higher values of energy. As electrons now populate states in the conduction band, the apparent value of the bandgap energy will increase, as now an electron excited from the ground state must be excited to an energy level above these occupied states. This effective increase in the bandgap is known as the Moss-Burstein shift [74].

![Illustration of semiconductor direct transitions and the Moss-Burstein band gap shift in n-type doped semiconductors](image)

**Figure 2.3** Illustration of semiconductor direct transitions and the Moss-Burstein band gap shift in n-type doped semiconductors

2.4.4. Laser absorption in Metals: The Drude Model

The contribution of the free carriers to laser absorption is important in metals, which have a large free carrier density. The Drude model is a conductivity model, which uses classical equations of motion of an electron in an electric field, to derive the optical properties including the absorption coefficient and the reflectivity [75].

The characteristic frequency at which the metal changes from metallic-like like properties to dielectric-like properties is known as the plasma frequency. This is given by
\[ \omega_p^2 = \frac{4\pi ne^2}{m\varepsilon_0} \]  

(7)

where \( n \) is the number density of electrons, \( m \) is the mass of the electron, \( \varepsilon_0 \) is the relative permittivity and \( e \) is the electronic charge. The absorption coefficient of the material according to the Drude model can be approximated from the imaginary part of the refractive index, \( \alpha = \frac{2\omega n_i}{c} \), which gives an absorption coefficient which goes as

\[ \alpha = \frac{\omega_p^2 v_e}{c(\omega^2 + v_e^2)} \]  

(8)

where \( v_e = \frac{1}{t_{e-i}} + \frac{1}{t_{e-n}} \) and \( \omega \) is the laser frequency. In this case \( t_{e-i} \) is the time between electron collisions and \( t_{e-n} \) is the time between electron-neutral collisions. This gives an absorption coefficient which is dependent on the square of the laser wavelength \( \lambda^2 \).

2.4.5. Fourier Heat Equation

The absorption of laser energy by a material leads to an increase in the internal energy \( \Delta E = \Delta U = c_p m \Delta T \), where \( \Delta E \) is the absorbed laser energy (J), \( \Delta U \) is the increase in the internal energy of the material, \( c_p \) is the heat capacity at constant pressure (J/kg K\(^{-1}\)), \( m \) is the mass of the material (kg) and \( \Delta T \) is the temperature rise (K). As the temperature rises, the kinetic energy of the atoms can overcome the binding energy, which gives a phase transition from the solid to the molten state. This energy required to overcome the binding energy is known as latent heat of fusion. If the temperature of the molten region is increased further, evaporation of the atoms away from the molten material can take place. This heating of a material can be described for long heat sources, such as nanosecond laser pulses, using the Fourier heat equation [76].
\[ [c_p + L_m \delta(T - T_m) + L_v(T - T_v)] \rho \frac{\partial T(x,y,x,t)}{\partial t} - \nabla[k\nabla T] = Q \] 

(9)

Where \( k \) is the thermal conductivity \((\text{Wm}^{-1}\text{K}^{-1})\), \( \rho \) is the material density \((\text{kgm}^{-3})\), \( T_m \) (K) is the melting temperature, \( T_v \) is the vaporisation temperature, \( L_m \) is the latent heat of fusion \((\text{Jkg}^{-1})\), \( L_v \) is the latent heat of vaporisation, \( Q \) is the laser source term \((\text{Wm}^{-3})\).

\( L_m \delta(T - T_m,v) \) is used to simulate the increase in heat capacity as the material undergoes a melting \((T_m)\) and vaporisation phase change \((T_v)\). The delta function \( \delta \) can be approximated by a Gaussian function [77]

\[ \delta(T - T_{m,v}\Delta) = \frac{1}{\sqrt{2\pi\Delta}} \exp\left[-\frac{(T - T_{m,v})^2}{2\Delta^2}\right] \] 

(10)

Where \( \Delta \) is a constant, typically in the range of 50-100 K, to allow a smooth transition to the latent heat region, as the lattice temperature increases. Analytical solutions to the heat equation can be found using methods of integral transformations and Greens function [78], however, finite element methods can also be used to directly solve the equation [79].

For a set of laser parameters, the temperature in the material depends on the optical absorption properties of the material and the transport of heat away from the excitation region. The laser source term for a pulse with Gaussian shapes in the radial and temporal domain \((r,t)\) can be described as [80]

\[ Q(r,z,t) = \frac{2\phi_0 \alpha(\lambda)}{\sqrt{\pi/\ln 2} \tau_p} (1 - R(\lambda))\exp\left[-\frac{2r^2}{\omega_0^2} - (4\ln 2)\left(\frac{t}{\tau_p}\right)^2 - (\alpha(\lambda)y)\right] \] 

(11)

Where \( \phi_0 \) is the peak applied incident fluence \((\text{J/cm}^{-2})\), \( \alpha(\lambda) \) is the absorption coefficient \((\text{m}^{-1})\), \( \tau_p \) is the FWHM pulse duration \((\text{s})\), \( R \) is the material reflectivity, and \( \omega_0 \) is the laser spot radius \((\text{m})\).

As the material absorbs the laser energy, the temperature of the material may exceed the melting temperature. In this case, the transition of the material from a solid to a molten phase take place. As the temperature is increased further towards \( T_v \), evaporation of particles from the molten material can take place. If the recoil pressure gradient from evaporation is large enough to overcome surface tension forces the molten particles, the
particles will be ejected away from the material [81]. The recoil pressure $p_r$ is given as the saturated vapour pressure taken from the Claus Clapeyron equation [82]

$$p_r(T) = p_0 \exp \left[ \frac{L_v(T - T_v)}{(R_g TT_v)} \right]$$

(12)

where $p_0$ is the atmospheric pressure and $R_g$ is the gas constant. Due to the exponential functions, values of $p_r$ are in general only relevant as $T \rightarrow T_v$. The rate of atomic flux away from the surface can be taken from the Hertz Knudsen equation [82]

$$J_i = \frac{p_r(T)}{(2\pi m_i k_B T)^{1/2}}$$

(13)

where $J_i$ is the atomic flux (species/cm$^2$), $m_i$ is the mass of the species leaving the surface (kg), and $k_B$ is Boltzmann’s constant. Figure 2.4 shows the general surface geometry for the material surface under laser irradiation, with laser induced melt regions and surface recession due to particle flux away from the surface.

![Surface geometry after laser irradiation including melt region and surface recession due to particle flux away from the surface](image-url)
2.5. Ultrashort laser pulse absorption

As the pulse duration is decreased to the ultrafast time regime, (typically < 10 ps), the traditional Fourier equation breaks down, and does not adequately describe absorption in the material of the ultrafast laser pulse. Here material absorption is described in terms of the two temperature model, along with various non-linear absorption properties.

2.5.1. Two temperature model

The timescales of ultrafast laser absorption has been studied experimentally using femtosecond pump-probe reflection transmission techniques [83-86]. From this, the general process of ultrafast laser absorption can be characterised in three stages. In the first stage, the electronic sub-system absorbs the laser pulse, leading to an electron temperature which is established within 10-50 femtoseconds after the initial laser irradiation. High energy ballistic electrons can then penetrate further into the target bulk, for instance up to depths of 100 nm for gold [87]. The energy of the electrons is then coupled to the lattice phonons within a few ps after laser irradiation.

![Figure 2.5 Timescales of laser pulse absorption (fs laser pulse shown in red) and material reaction for ultrafast laser sources](image-url)

This process of ultrafast electronic absorption can be modelled using the now standard two temperature model (TTM) [88]. This defines the electronic and lattice as two separate subsystems, described by two coupled differential equations. The temperature of the electrons $T_e$ and lattice $T_l$ is given as
\begin{equation}
C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla (k_e(T_e) \nabla T_e) - G(T_e - T_i) + Q \tag{14}
\end{equation}

\begin{equation}
C_l(T_l) \frac{\partial T_l}{\partial x} = \nabla (k_l \nabla T_l) + G(T_e - T_l) \tag{15}
\end{equation}

where \(C_e, C_l\) are the specific heat capacities of the electrons and lattice (J/m\(^3\)K), \(k_e, k_l\) are the heat conductivities of the electrons and lattice (J m\(^{-1}\)s\(^{-1}\)K\(^{-1}\)) and \(G\) is the electron phonon coupling factor (J m\(^{-3}\)s\(^{-1}\)K\(^{-1}\)), and \(Q\) is the laser source term. An estimation of the electronic heat capacity and its dependence on the electron temperature, is given by a linear dependence \(C_e = C_0 T_e\) [83] where \(C_0\) is given as

\begin{equation}
C_0 = \frac{\pi^2 n k_B}{2 T_F} \tag{16}
\end{equation}

where \(n\) is the density of electrons (m\(^{-3}\)), \(k_B\) is Boltzmann’s constant, and \(T_F\) is the Fermi temperature given as \(T_F = E_F / k_B\). This approximation is generally valid in region of \(0 < T_e < T_f\). The thermal conductivity of the electrons is given as

\begin{equation}
k_e(T_e, T_l) = v^2 C_e(T_e) \tau_e(T_e, T_l) / 3 \tag{17}
\end{equation}

where \(v^2\) is the mean squared velocity of the electrons (m\(^2\)s\(^{-2}\)) contributing the thermal conductivity of the electrons. This can be approximated as \(v^2 = v_F^2\), where \(v_F\) is the Fermi velocity, where \(v_F = \sqrt{2E_F / m}\). \(\tau_e\) is the electron scattering time, including contributions from electron-electron and electron-phonon scattering. \(1/\tau_e = 1/\tau_{e-e} + 1/\tau_{e-ph}\). The electron phonon coupling factor \(G\) can be approximated as [89]

\begin{equation}
G = \frac{\pi^2 m_e^* c_s^2 n_e}{6 \tau_e(T_e) T_e} \tag{18}
\end{equation}
where \( m_e^* \) is the effective mass of the electron, \( c_s \) is the speed of sound, given as \( c_s = \sqrt{\beta / \rho} \), where \( \beta \) is the bulk modulus and \( \rho \) is the density, \( \tau_e \) is the electron relaxation time. The original two temperature model has a number of limitations in the constants used. A number of studies have attempted to improve the two temperature model. In the two temperature model, the electronic heat capacity is normally assumed to have a linear relationship with the electronic temperature, absorption coefficient, electron heat capacity and absorptivity. Recent studies have concentrated on delivering a better estimation of these constants through quantum mechanical derivations [90]. This allows for more accurate simulation of the temperature of the electrons and lattice for ultrashort pulses.

2.5.2. Non-linear absorption using ultrafast laser pulses

Absorption of ultrafast pulses in some materials can lead to a number of non-linear absorption effects, such as multiphoton ionisation, avalanche ionisation and impact ionization. These processes are important for wide bandgap dielectrics and semiconductors, where the incident photon energy is often less than the bandgap energy. These materials are transparent for low intensity pulses with wavelengths in the visible wavelength range. Non-linear absorption can lead to localised damage in dielectrics [91-93], which may be relevant to thin films deposited on dielectric substrates. In order for laser pulse absorption to take place, sufficient densities of electrons must be generated in the conduction band. Multiphoton ionisation occurs due to the simultaneous absorption of multiple photons by a valence band electrons. The onset of multiphoton ionisation can be described by the Keldysh parameter

\[
\gamma = \frac{\omega}{e} \sqrt{\frac{m_e^* c \varepsilon_0 n E_g}{I_0}}
\]  
(19)

Where \( m_e \) (kg) is the mass of the electron, and \( \varepsilon_0 \) is the relative permittivity of the material, \( I_0 \) is the peak laser intensity (W/m\(^3\)), \( c \) is the speed of light and \( \omega \) is the laser frequency. Avalanche ionisation occurs due to during free carrier absorption, where ionisation of further carriers can take place by impacting valence electrons. In order for this to take place, typically seed electrons are required, normally originating from defect states and colour centres in the material. The valence electrons exciting to the conduction

24
band leads to a cascade effect, increasing the electronic density in the conduction band. The density of electrons in the conduction band has a major effect on the absorption level of the incident laser pulse, as the free electrons in the conduction band are now free to absorb the laser energy. The absorption coefficient for the free electrons can be approximated by the Drude model described by (8). Overall the interplay between the non-linear and avalanche effects leads to an electronic rate equation which describes the electron density as a function of various non-linear absorption properties [94]. In order for absorption in the dielectric conduction band to take place, the density of electrons in the conduction band must overcome a critical density ($\sim 10^{21} cm^{-3}$) [95]. This critical density of electrons is often used in thermal simulations, to define the ablation region in dielectrics using ultrashort pulses. It has been shown, that when a region has a density over the critical density of electrons, ablation of that region takes place. This has been compared to standard thermal models, and good agreement has been obtained between the simulated and experimental ablation depths. [96].

2.6. Material threshold fluence

The laser threshold fluence, given in J/cm², is the critical energy defined as the visible onset of material damage. The threshold fluence for any material is typically measured using Liu’s method [97]. Using this method, the focussed Gaussian spot radius can be measured by examining the variation in crater diameter with incident laser pulse energy. Once the spot radius is obtained, the incident fluence can be found, for any given laser pulse energy. These standardised fluence values allow comparison of laser processing across different materials and wavelengths.

The threshold fluence in general, has been found for a given material to vary with incident laser wavelength [98]. This is due to the change in absorption in the material for various wavelengths. Certain wavelengths will have increased absorption due to certain optical properties of the material. In the case of polymers, UV wavelengths allow direct photochemical bond breaking of the polymer chains, due to direct absorption of the photon by the molecular bond [99].

The threshold fluence is measured in terms of an applied energy density, is therefore normalised to the applied spot radius. This is typically a fixed parameter, and the dependence of the threshold fluence is not normally dependent on the applied laser spot
radius. Variations in the multi-pulse threshold fluence with laser spot radius have previously been studied for femtosecond ablation of dielectrics [100, 101]. A defect dominated mechanism was used to describe the change in the fluence threshold in these cases. Ablation in the dielectric was assumed to be initiated through defects in the material. Larger spot radii were modelled as having a greater chance of encountering a defect, therefore having a greater probability of initiating ablation in the spot radius area, thus decreasing the threshold fluence. Ablation plume shielding effects can also play a role in changing the threshold fluence with spot radius. Studies using excimer lasers on silicon [102] and polymers [103], have shown decreases in the threshold fluence with increasing spot radius, due to variations in plume shielding with the incident spot size.

The pulse duration is another key characteristic in the overall value of the threshold fluence. In general, decreasing the pulse duration results in lower threshold fluences. The threshold fluence in general has a linear decrease in the nanosecond to the high picosecond time regime. This is primarily due to the energy loss due to diffusion if thermal energy is transported away from absorption area during the laser pulse duration. This leads to a dependence of the threshold fluence on the laser pulse duration. \( F_{th} \propto \sqrt{\tau_p} \) [104]. As the pulse duration is decreased further to the low picosecond and femtosecond pulse durations, the threshold deviates from this trend. The high intensity laser pulses lead to non-linear effects in the material, changing the laser absorption and ablation mechanisms.

2.7. Material ablation and removal

The removal of material after laser irradiation can take place through numerous methods, which have a dependence on parameters such as the laser wavelength, pulse duration, applied fluence and material properties. Typically the laser material interaction can be separated into thermal interactions, where the removal method is due to local heat rise followed by melting and vaporisation, and non-thermal removal, where the ejection of material takes place to a relatively cold lattice.
2.7.1. Laser-material thermal interaction

After laser energy is deposited in the material, typically heating of the lattice takes place on a picosecond time scale. The temperature increase with time can be estimated by the Fourier heat equation, given by equation (9). A number of competing processes can then place, including surface melting and evaporation, surface vaporisation, plasma ejection and heat diffusion. These processes depend on a number of parameters including laser pulse duration, wavelength and the material parameters.

The initial energy deposition in the material take place within an absorption depth of \( d_\alpha = \frac{1}{\alpha(\lambda)} \), where \( \alpha(\lambda) \) is dependent on the material and the applied laser wavelength. As the laser beam is absorbed in the material, heating of the lattice will take place on a picosecond to nanosecond time scale. The temperature profile in the material will be Gaussian across the laser absorption region, where the laser radial profile is Gaussian. As the temperature in the material rises, the temperature gradient in the material is established, resulting in the diffusion of heat with a gradient given by

\[
\rho c_p \frac{\partial T}{\partial t} = k \nabla^2 T
\]  

The heat diffusion length in the material is given by \( l_t = \sqrt{2D\tau_p} \), where \( D \) is the heat diffusivity given by \( D = k/\rho c_p \) [105]. The heat diffusion length has a direct dependence on the material properties but more importantly, the pulse duration of the laser used. The heat diffusion length has been shown to play a major role in the defining laser ablation of
thin films in particular. It has been shown for polymer films, that the relationship between the film thickness and the heat diffusion length, has a large impact on the material threshold fluence [105]. The threshold fluence increases linearly for film thicknesses up to the heat diffusions length. After this point, no change in the threshold fluence is seen with increasing film thickness.

If the temperature becomes greater than the melting point, phase change to a molten liquid will take place. A melt front will then propagate into the material, at speeds in the region of a few hundred metres per second [106]. The dynamics of the melt front after laser heating can be examined using molecular dynamic simulations, and the characteristic properties of the melt can be extracted [107]. Fluid flow in the melt develops as the melt front propagates. This is due to the surface tension properties of the molten material, which has a temperature dependence $\gamma(T)$. The surface tension in the radial direction of the pulse has a distribution that is Gaussian, for laser pulses with a Gaussian radial intensity profile

$$\frac{\partial \gamma(r, T)}{\partial r} = \frac{\partial \gamma(r, T)}{\partial T} \frac{\partial T(r)}{\partial r}$$

(21)

Where $\gamma(r, T)$ is the surface tension, and $\partial T/\partial r$ is the temperature gradient in radial direction. Molten fluid flow may take place in the material after laser irradiation, which drives molten material to areas of higher surface tension [108, 109]. Due to the Gaussian spatial distribution of the incident laser pulse, molten material is driven from the centre to the crater edge, where re-solidification takes place on cooling, once the material drops below the melt temperature. Molten fluid flow has been analysed experimentally for nickel films, using nanosecond laser sources [110], and for silica glass, using femtosecond pulses [111]. The simulation of molten fluid can be analysed using the Navier-Stokes equation, which examines thermo-capillary stresses in the molten region [112].

If the applied fluence is such that the temperature reaches the vaporisation temperature of the material, the transition of the material from a liquid to gas phase can take place [113]. The ejected material can be classified into two parts. The laser induced plasma consisting of ejected electrons and ions, and a particulate component. The ejection of the plasma takes place typically within the first 100 nanoseconds after laser irradiation. The initial
plasma velocity can easily reach 10,000 m/s and disperse to large distances from the material surface. The plasma characteristics are determined by a number of factors, including the pulse duration, spot radius, numerical aperture, material properties and the ambient atmosphere composition and pressure [114]. The propagation of the laser plasma and shockwave can be approximated by point blast theory, where the plasma front position \( R \) depends on [115], from the centre of the laser spot at the surface, given by

\[
R = (eE\rho_g)^{3/5} \tau^{2/5}
\]  

(22)

Where \( E \) is the energy released in the explosion (J), \( \rho_g \) is the density of the background gas, and \( e \) is a constant. As a result, the ongoing nanosecond pulse can interact with the ejected plasma, typically resulting in attenuation of a portion of the laser energy [116]. This attenuation can cause a variation in the applied threshold fluence, as the spot radius defines the ejection aperture of the plasma from the material [102]. Plume visualisation through shadowgraphy techniques [117] allows the characteristics such as plume height and plume front velocity to be obtained. The evolution of the plasma can be modelled using both a shockwave model and drag model [118]. Computational simulations using numerical techniques [119], can be used to model the plasma temperature, height, velocity and other components.

Assuming sufficient energy is imparted to the material, removal of the nanoparticles and molecules from the surface can take place. The mechanism for material removal is dependent on many factors, including applied laser characteristics, along with the material properties. Material removal in general can be classified as thermal or non-thermal mechanisms.

Removal of the material via thermal effects can typically be split into three categories, such as phase explosion, vaporisation, and boiling [120, 121]. The relevance of each process depends on the interaction of the laser pulse with the material, with the important parameters being the pulse duration and applied fluence.

Phase explosion occurs when the material region is rapidly heated to the limit of superheating \((0.9T_c)\), where \( T_c \) is the thermodynamic critical temperature (Gold = 8970 K). The superheated liquid loses stability, and homogenous nucleation of the vapour phase takes place throughout the melt, leading to a gaseous expansion into the ambient [122].
This results in a rapid transition from superheated liquid to vapour and liquid droplets. This type of thermal ablation mechanism is generally favoured for material removal using ultrashort laser pulses at moderate fluences [123]. This is due to the timescales of ultrafast laser absorption. If the increase in temperature of the molten material is slow, it will follow the bimodal line on the phase temperature diagram (p-T), with the material following a series of equilibrium states described by the Clausius-Clapeyron equation. Figure 2.7 shows the typical pressure-temperature phase diagram region of the critical point. The bimodal line, given as 1 in Figure 2.7, shows the equilibrium point between the liquid and vapour for both pressure and temperature.

Figure 2.7 Typical liquid-vapor phase diagram showing the bimodal phase line (1) and the spinodal phase line (2)

If the molten phase undergoes sufficient heating, a superheated liquid can be formed, with the system shifting close to the spinodal line. The phase explosion process is therefore highly dependent on the applied laser fluence, as the deposited energy must be large enough to bring the surface temperature to the critical temperature, but low enough to allow controlled heating of the molten phase. A second factor which has a large effect on the presence of phase explosion is the applied laser pulse duration. It has been proposed that phase explosion can only take place using femtosecond laser pulses, with picosecond laser pulses too long to initiate this process [124]. When the melt is heated using picosecond laser pulses, heat conduction will take laser energy away from the ablation region, resulting in a shift in temperature away from the spinodal line. This has been
observed for femtosecond and picosecond pulses using molecular dynamics simulations [125]. Pulses longer than a few picosecond result in fragmentation of the associated melt due large strain rates in the rapidly heated melt. Fragmentation is essentially a strain related expulsion of material. However, as it takes place in a highly heated melt, it can also be considered thermal in nature.

Thermal material removal can also occur through homogenous and heterogeneous boiling occurs within the material, beginning at nucleation regions in the material. These nucleation points typically form at defect states in the material, especially at regions between the solid and liquid phase [126].

As the pulse duration is increased to the nanosecond time regime, the thermal removal process of the material changes, with access to critical temperature states impeded by thermal conduction. The thermal pathway, which defines the transition from solid to liquid and vapour, follows the bimodal line shown in Figure 2.7 as the pulse duration is increased into the nanosecond time regime. As the temperature is increased, the molten material undergoes a recoil pressure described in equation (12). This recoil pressure leads to a surface recession velocity of particles away from the surface, described by the Hertz-Knudsen equation given in equation (13). Vaporisation has been shown to be a dominant thermal material removal method using nanosecond pulses for materials such as semiconductors [127] and metals [128].

2.7.2. Laser material non-thermal interaction

Ejection of material due to mechanical effects can play a role in the removal of material, depending on the material conditions and laser pulse properties. This mechanical removal of material may take place at much lower temperature conditions than those required for material melting or evaporation. In general, mechanical ejection of the material is due to the stress build up in the material. As materials heat up, thermal expansion of the material can take place, with a displacement given as $\Delta L$ in each dimension. The normalised deformation of the material is defined as strain, given as $\Delta L/L$. The heating of materials leads to thermal expansion, which can gives rise to a strain in the material. When the material cannot expand, this results in an associated stress. Firstly, the strain tensor can be written in terms of the displacement gradients
\[ \varepsilon_{mech} = \frac{1}{2} [ (\nabla u)^T + \nabla u ] \]  

(23)

Where \( \varepsilon_{mech} \) is the material strain, and \( \nabla u \) is the displacement field. The strain tensor can be given in the most general form by nine different tensor elements, given as

\[
\begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
\varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\
\varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz}
\end{bmatrix}
\]  

(24)

These strain tensors are shown in Figure 2.8.

Figure 2.8 Strain tensors along the x, y and z axis

Taking into account a 2D axis distribution and symmetry, the nine tensors reduce to two tensile tensors, \( \varepsilon_{xx} \) and \( \varepsilon_{yy} \), and one shear tensor element \( \varepsilon_{xy} \). The stress in the material is related to the strain via the Duhamel-Hooke’s Law

\[ \sigma - \sigma_0 = C : (\varepsilon - \varepsilon_0 - \varepsilon_{th}) \]  

(25)
Where $\sigma_0$ and $\epsilon_0$ are the initial stress and strain respectively and $\epsilon_{th}$ is the thermal strain, given as $\epsilon_{th} = \alpha_T(T - T_{ref})$, where $\alpha_T$ is the expansion coefficient and $T_{ref}$ is a reference temperature, typically given as room temperature.

$C$ is a 4th order elasticity tensor where $:$ stands for the double dot tensor product. The 4th order elasticity tensor is used to relate the linear relationship between strain and stress, which are both 2nd order tensors. In general, 4th order tensors are used to relate a combination of two second order tensors. Using condensed notation, the overall six independent components of stress and strain can be written as

$$
\begin{align*}
\sigma_{xx} &= (\lambda + 2\mu)\epsilon_{xx} + \lambda\epsilon_{yy} + \lambda\epsilon_{zz} \\
\sigma_{yy} &= \lambda\epsilon_{xx} + (\lambda + 2\mu)\epsilon_{yy} + \lambda\epsilon_{zz} \\
\sigma_{zz} &= \lambda\epsilon_{xx} + \lambda\epsilon_{yy} + (\lambda + 2\mu)\epsilon_{zz} \\
\sigma_{yz} &= 2\mu\epsilon_{yz} \\
\sigma_{zx} &= 2\mu\epsilon_{zx} \\
\sigma_{xy} &= 2\mu\epsilon_{xy}
\end{align*}
$$

(26)

The two parameters $\mu$ and $\lambda$ can be described using measurable elastic properties of materials. In the case of Young’s Modulus $E$ and Poissons Ratio $\nu$

$$
E = \frac{(3\lambda + 2\lambda)\mu}{(\lambda + \mu)}
$$

$$
\nu = \frac{\lambda}{2(\lambda + \mu)}
$$

(27)

De-lamination is a film removal process often associated with thin films. The general process for this removal method consists first of heating of the film and substrate, which results in sudden material expansion, this generates strain in the film and substrate, often with peak values at the interface between the film and substrate. This strain generates an associated stress in the film, which can exceed the bond strength and result in fragmentation of the film away from the substrate. This has been observed for laser processing of metal thin films such as Molybdenum and Chromium [129], dielectric layers on silicon [130] and TCO’s on flexible polymer substrates [131]. The fragmentation of material occurs due to the high stress generated, which can typically be
of the order of MPa [132]. The exact nature of the stress depends on the thermal expansion properties of the film and substrate materials.

The generation of stress in materials particularly occurs using ultrashort laser pulses. Due to the highly non-equilibrium hot electrons, a transient elastic stress is formed in the lattice, known as the hot electron blast force. This generates a pressure wave in the lattice which expands to a depth of the material at the velocity of sound [133-135]. The electron blast force has been modelled using the Boltzmann equation and the Fermi-Dirac partition function. The linearly elastic equations of motion for ultrafast lattice deformations are given as [136]

\[
\rho \frac{\partial^2 u_i}{\partial t^2} = \lambda_{ijmn} \frac{\partial^2 u_m}{\partial x_j \partial x_n} + B_i
\]  

(28)

Where \( \rho \) is the lattice density, \( u_i \) are the displacement components, \( \lambda_{ijmn} \) are the elastic constants, and \( B_i \) is the electron blast force component. The electron blast force component is given as

\[
B_i = 2\Lambda_{ij} T_e \frac{\partial T_e}{\partial x_j} , \Lambda_{ij} \sim g C_o \delta_{ij}
\]  

(29)

Where \( \delta_{ij} \) is the Kronecker delta function, \( g \sim 1 \) is a dimensionless electron phonon coupling constant and \( C_o \) is the characteristic constant for the electron heat capacity. This leads to direct dependence between the electron blast force and the gradient of the electronic temperature. This ultrafast deformation has attracted significant interest with regards to femtosecond laser irradiation with metal thin films [137-139].

Coulomb explosion is a mechanism typically associated with ultrafast laser pulses, and materials such as dielectric and semiconductors [140]. Using ultrafast, high intensity laser pulses, ejection of electrons through photo-emission or thermionic emission takes place before thermalisation between the electrons with the lattice. This leaves unshielded positively charged atoms in the material. The repulsive forces between the atoms can exceed the binding energy of the bonds, resulting an explosive repulsion between the atoms. Comparing the binding energy of an atom with an electric field corresponds to the
volume occupied by an atom. this gives the threshold electric field required for Coulomb explosion [141]

\[ E_{th} = \sqrt{2\Lambda_{at} n_a/\varepsilon_0} \]  

(30)

Where \( \Lambda_{at} \) is the latent heat of vaporisation of a single atom, \( n_a \) is the number density of the material. This gives electric field thresholds for most materials in region of \( 10^{10} V/m \). Coulomb repulsion has been shown to be an important ablation mechanism for semiconductors [142] and dielectrics [143]. The removal of material by Coulomb explosion for metal targets still remains under consideration [144].

2.7.3. Surface modifications: Ripple structures

Another surface feature noted for both nanosecond and ultrafast pulses, across a wide range of materials, is laser induced periodic structures (LIPPS). These self-organised structures, with a ripple like pattern, are typically observed upon laser irradiation with multiple pulses with an applied fluence at or below the threshold fluence. These ripple structures have been observed on silicon [145], glass [146], metals [147], semiconductors and polymers [148]. The original theory for LIPPS formation was proposed to the interaction of radially scattered incident light waves from surface. The theory indicates that this results in ripples with a period of

\[ \Lambda = \frac{\lambda}{n_{eff} \sin \theta} \]  

(31)

Where \( \lambda \) is the laser wavelength, \( \theta \) is the angle of incidence, and \( n_{eff} \) is the refractive index of the material. This results in ripples with a period of between \( \lambda \) and \( \lambda/2 \), known as low spatial frequency LIPPS. The exact method for the formation of ripples is still under debate in the literature. Due to the Gaussian spatial intensity, different ripple periodicities can be observed between the crater edge and the crater centre. High frequency LIPPS are also observed at the crater edge, when diameters of ripple structures are much smaller than the laser wavelength. Other theories have focussed on self-organisation [149] and surface plasmons [150].
2.7.4. Multiple laser pulses and incubation

The irradiation of the sample material with multiple subsequent pulses results in changes to the material topography and the threshold fluence. The threshold for subsequent pulses can drop below the threshold for a single laser pulse. Typically, the lowering of the threshold fluence is described by the following empirical power law equation [151], given by

\[ \phi_{th}(N) = \phi_{th}(1)N^{S-1} \]  

(32)

Where \( \phi_{th}(N) \) is the threshold fluence after \( N \) pulses, \( \phi_{th}(1) \) is the threshold fluence for one pulse, \( \phi_{th}(N) \) is the threshold fluence for the \( N^{th} \) pulse, \( N \) is the number of pulses and \( S \) is the incubation parameter. This theory implies a decrease in the threshold fluence with increasing number of pulses, when the \( S < 1 \).

2.8. Laser removal of ITO films

The characteristics of laser patterned ITO films have been studied at different wavelengths and pulse durations, however typically these studies have focused on selective removal of the film, with thicknesses of 100 – 500 nm, and not on the fundamental ablation processes themselves. Furthermore, no real insight into the pulsed laser absorption mechanisms, or in-depth analysis of the surface topography has been carried out to date. The influence of wavelength has been noted as a factor in the selective removal of the ITO film, in the case where overlapped pulses are used to create a line. ITO films of 150 nm thickness were selectively patterned using ns laser sources at 1.047 \( \mu \text{m} \) [152], but smooth ripple free trenches were achieved at UV and deep UV (DUV) wavelengths at 0.349 and 0.262 \( \mu \text{m} \) [153]. Insufficient information on the surface topography of the trenches was given to confirm complete selective removal of the film with no glass damage. DUV 157 nm excimer pulses have also been used to pattern 100 nm thick ITO films, however damage to the glass substrate of 40 – 50 nm can be noted in the study [154]. Picosecond laser sources at 355, 355, and 532 nm were used to selectively remove 120 nm thick ITO films [155]. 266 nm was identified as the optimal
laser source for clean film removal. The removal of 150 nm ITO films from soda limes glass was also investigated using an IR femtosecond laser, across a range of repetition rates and scan speeds. The threshold fluence of the ITO film was found to be dependent on the laser spot radius, however, only two spot radii were tested.

Laser patterning experiments on ITO deposited on PET, have also been carried out previously in the literature. Typically these have only focussed on selective removal of the film and laser pulses overlapping to create lines, with typical film thicknesses of 100 – 500 nm. The removal of 120 nm thick ITO on PET has been studied for nanosecond laser pulses at a wavelength of 1064 nm [156]. Shadowgraphy was used to estimate the fragment velocity away from the surface. Fragment velocities were in the range of 200-400 m/s, indicating a potential delamination film removal mechanism. Selective removal of the ITO film has been achieved using excimer ablation of 300 nm films achieved at 246 nm [157]. Due to the short wavelength used, thermal evaporation of the ITO was proposed as the film removal mechanism. Selective removal of 100 nm thick ITO film from the PET substrate has been obtained for picosecond pulses, at wavelengths of from 343, 532 and 1030 nm [158].

### 2.9. Laser ablation of polymers

The interaction of laser pulses with polymer materials has been studied extensively in the literature. Currently the mechanisms of laser ablation for polymers is still debated, with laser wavelength found to play a key role in the ablation properties of the material.

Two process of laser polymer are interaction are generally considered for UV laser pulses. The first mechanism is through photo-chemical ablation [159], where absorption is through high energy photons by the polymer chain bonds, which can lead to direct bond breaking in the material. Material removal can then place due to an increase in the local particle density, which results in a rise in the local pressure. The resultant pressure release is accompanied by a shockwave, which can lead to the ejection of the polymer as a monomer or in a gaseous state. The timescales for the photo-chemical reaction take place quicker than for the excited state thermalisation, resulting in a non-thermal ejection process. Laser ablation of polymers via thermal methods such as melting and vaporisation can also take place [160].
2.10. Summary

This review of the relevant literature within the laser material interaction area, has highlighted some of the current topical areas, along with some gaps in the literature. Overall, the interaction properties of thin TCO films with nanosecond and ultrashort laser pulses are still not widely understood. A number of key issues remain, in terms of a lack of understanding of the fundamental film removal mechanisms across a range of laser parameters, such as pulse duration, wavelength, spot overlap, and laser spatial intensity profile. The effect of substrates on the film removal properties, along with the mechanisms for substrate damage is also not widely understood.

Hence the objective of this study is

- Identify key issues pertaining to the absorption of laser energy in very thin ITO films
- Clearly identify the surface topography for ablation of very thin ITO films experimentally
- Use this data and other numerical simulations to identify the ITO thin film removal mechanisms
Chapter 3

3. Equipment, Materials, and Methods

This chapter contains descriptions of the various lasers and characterisation techniques used for thin film ablation. The laser machining setup across the pulse durations and wavelengths typically consists of a laser source, a beam delivery method, and laser parameter control. A small number diagnostic and characterisation tools were used to analyse and visualise the laser-material interaction. Information on the thin film and substrate materials used in this study is given in this chapter. A full detailed description of the computational finite element simulations is given, including the material constants and assumptions used.
3.1. Laser Sources

3.1.1. Generation of nanosecond laser pulses

A very brief overview of the generation of nanosecond pulses is presented. In order to generate pulsed laser light in a solid state system, a population inversion in a 4 level structure is typically used. In order to achieve a population inversion in the gain medium, the medium must be pumped with another energy source. This gives the three main components of short pulse laser generation, the gain medium, the optical cavity and the pump source. The gain medium is placed in the optical cavity, which typically consists of a doped crystal. The optical resonant cavity consists of two resonator mirrors which reflect the light in the desired range of wavelengths. The laser oscillates in a narrow range of frequencies around the transition frequency. This gain profile has a typically Gaussian distribution around the molecular line transition. A standing electromagnetic wave will propagate in the cavity, with longitudinal modes at the resonance condition \( v_m = mc^2/L \), where \( m \) is an integer, \( c \) is the speed of light, and \( L \) is the length of the cavity. The cavity longitudinal modes overlap with gain profile to create the laser output spectrum. The output of the laser pulse with a nanosecond pulse durations is controlled through Q-switching. This rate controls the laser frequency output of the laser.

![Typical laser cavity for nanosecond pulse duration](image)

The nanosecond lasers of interest in this study are \( Nd:YAG/Nd:YVO_4 \) nanosecond lasers, which use a diode laser at 808 nm to pump \( Nd^{3+} \) ions doped in a yttrium/crystalline matrix. The principal absorption band is in the red and near-infrared, as shown in Figure 3.2, which is shown for a \( Nd:YVO_4 \) nanosecond laser used in this study.
The most likely energy transition is to the $I_{1/2}$ level, which results in the emission of a photon with a wavelength of 1064 nm. Most solid state lasers output in $TEM_{00}$ mode, which is the most efficient mode, which maximises the overlap of the regions of the active medium and pumping source. The fundamental wavelength can be changed using a technique known as high harmonic generation (HHG). Harmonic generation is a non linear effect in specific materials, for example Lithium Niobate. Typically the wavelength is alerted to $\lambda/2, \lambda/3$ or $\lambda/4$.

3.1.2. Nanosecond 355 nm Pulsed Laser Source

The laser source used at an output wavelength of 355 nm, was a Coherent Avia diode pumped solid state laser (DPSS) laser. Table 1 shows the supplied technical specifications supplied by the vendor.
Table 1 Laser parameters for the 355 nm nanosecond Coherent Avia laser

<table>
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<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
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<tr>
<td>Wavelength</td>
<td>355</td>
<td>nm</td>
</tr>
<tr>
<td>Pulse Width</td>
<td>20</td>
<td>ns</td>
</tr>
<tr>
<td>Average Power Output</td>
<td>4.5 @ 25 kHz</td>
<td>W</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>10 – 100 kHz</td>
<td>kHz</td>
</tr>
<tr>
<td>Spatial Mode</td>
<td>TEM₀₀ (M² &lt; 1.3)</td>
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<tr>
<td>1/e² Beam Diameter</td>
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<td>mm</td>
</tr>
</tbody>
</table>

The 355 nm harmonic is generated using a Sum-Frequency Generation (SFG) of the fundamental 1064 nm photon, and second harmonic 532 nm photon, in a non-linear crystal. The population inversion is generated by the laser diode, which emits at 808 nm. The temperatures of the diodes, THG and SHG can be optimised using an automated internal calibration, along with the position of the laser on the crystal gain medium. This allows optimisation of a number of laser parameters, such as pulse to pulse instability, beam circularity, and peak power.

The optical setup of the laser system is shown in Figure 3.3. The output of the laser is first put through a rotary half-wave plate and beam splitting cube, which is used to externally control the laser power. This is advantageous, as it allows the diode current of the laser to be kept stable, limiting the pulse to pulse instability of the laser by keeping the variation in the cavity conditions at a minimum. A telescopic beam expander is used to expand the laser by a variable factor, typically in the range of 1–4. A spatial aperture was used to improve the beam circularity. It also defines the beam diameter and numerical aperture of the system. The focussing and scanning element used is a galvanometer (Scanlab Hurryscan) and an F-Theta lens (Sill Optics, 103 mm). The galvanometer is controlled using laser marking software (Winlase). The Winlase software allows dynamic vector marking. Laser scanning can be performed with marking speeds ranging from 30 – 2000 mm/s. The feature line length can be ranged from approximately 0.1 to 50 mm. The position of the sample is controlled using an x, y, z mechanical stage. The sample position was optimised at the focal point, by adjusting the z height until the focussed laser craters achieved the best circularity and smallest size.
Figure 3.3 Schematic diagram of the experimental configuration for the 355 nm Avia laser system, consisting of external attenuator, beam expander, variable aperture and focusing optics.

The optical properties of laser setup used for ITO thin film patterning are shown in Table 2.

Table 2 Optical configuration of 355 nm nanosecond laser pulses for ITO thin film patterning

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Pulse Duration (ns)</th>
<th>Repetition Rate used (kHz)</th>
<th>Raw Beam Output (mm)</th>
<th>Beam Expansion Factor</th>
<th>Aperture Size (mm)</th>
<th>Focal Length (mm)</th>
<th>NA</th>
<th>Spot radius (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>20</td>
<td>20</td>
<td>3.5</td>
<td>2.5</td>
<td>3-8</td>
<td>103</td>
<td>0.009 – 0.039</td>
<td>6.5 – 22.7</td>
</tr>
</tbody>
</table>
3.1.3. Nanosecond multi wavelength HIPPO laser source

In order to generate nanosecond pulses at wavelengths of 266, 523 and 1064 nm, an alternate nanosecond laser was used. This consisted of a Spectra Physics High Peak Power Oscillator (HIPPO), with a fundamental wavelength of 1064 nm. Frequency doubling modules could be attached to the laser head, in order to generate 266, 355 and 532 nm laser pulses. Two diode lasers operating at a wavelength of 808 nm, are used to pump the Nd:YVO₄ active medium. The laser operates with a $TEM_{00}$ output spatial intensity. An acousto-optic Q-switch in the cavity can be used to vary the repetition rate of the laser from 30-300 kHz. The laser power must be optimised for each wavelength in use. This is achieved by monitoring the laser output using a power meter, and adjusting the temperature of the harmonic modules in the laser software. The manufactures specifications of the laser is shown in Table 3.

Table 3 Manufactures specifications for the HIPPO nanosecond laser system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>266 nm</th>
<th>532 nm</th>
<th>1064 nm</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Width</td>
<td>8.6</td>
<td>9</td>
<td>9.2</td>
<td>ns</td>
</tr>
<tr>
<td>Average Power Output</td>
<td>2 W @50 kHz</td>
<td>11 W @50 kHz</td>
<td>17 W @50 kHz</td>
<td>W</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>15-300</td>
<td>15-300</td>
<td>30-300</td>
<td>kHz</td>
</tr>
<tr>
<td>Spatial Mode</td>
<td>$TEM_{00}$</td>
<td>$TEM_{00}$</td>
<td>$TEM_{00}$</td>
<td></td>
</tr>
<tr>
<td>$M^2$</td>
<td>&lt; 1.5</td>
<td>&lt; 1.3</td>
<td>&lt; 1.2</td>
<td></td>
</tr>
<tr>
<td>1/e² Beam Diameter</td>
<td>0.6</td>
<td>1</td>
<td>2</td>
<td>mm</td>
</tr>
<tr>
<td>Pulse –Pulse Instability</td>
<td>&lt; 8 %</td>
<td>&lt; 5 %</td>
<td>&lt; 2 %</td>
<td></td>
</tr>
</tbody>
</table>

The optical setup of the HIPPO laser system is similar to that shown in Figure 3.3. In the case of 266 nm laser pulses, a telescopic beam expander is used expand the laser beam by a factor of 5. A spatial aperture was then used to improve the beam circularity, along with defining the beam diameter. The raw laser beam is used in the case of 532 and 1064 nm pulses. The focussing element used various galvanometer (Hurryscan) and an F-Theta telecentric lenses (103 mm). The galvanometer is controlled using laser marking software (Winlase). The Winlase software is connected to the laser through an RC232 card, which inputs the signal for the internal gate. The position of the sample at the focal point is
controlled using an x, y, z mechanical stage. The optical configuration across the range of wavelengths is shown in Table 4, used for ITO thin film patterning.

Table 4 Laser optical system layout for the multiple wavelengths used for laser processing of ITO thin films using the HIPPO nanosecond laser system

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Pulse Duration (ns)</th>
<th>Repetition Rate used (kHz)</th>
<th>Raw Beam Output (mm)</th>
<th>Beam Expansion Factor</th>
<th>Aperture Size (mm)</th>
<th>Focal Length (mm)</th>
<th>NA</th>
<th>Focussed Spot radius (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>266</td>
<td>8.6</td>
<td>30</td>
<td>2.5</td>
<td>5</td>
<td>7</td>
<td>103</td>
<td>0.033</td>
<td>5.7</td>
</tr>
<tr>
<td>532</td>
<td>9</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>103</td>
<td>0.026</td>
<td>13.5</td>
</tr>
<tr>
<td>1064</td>
<td>9.2</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>103</td>
<td>0.026</td>
<td>22.7</td>
</tr>
</tbody>
</table>

3.1.4. Picosecond pulse generation

In a picosecond laser system, pump light is generated by a laser diode at a wavelength of 940 nm. The pump light is then delivered by an optical pump fibre cable, which allows flexible transmission between the pump module to the laser head. A mode locked seed laser is introduced to an amplifier pumped by a diode laser. Firstly the pump diode laser energy is homogenised by fibre coupling. The pump energy is focussed onto the disk, with unabsorbed energy re-focussed back on to the disk by a parabolic mirror. The disk itself is typically in the region of 100-200 μm in thickness, and a few millimetres in diameter. Upwards scaling of the laser power can be achieved by using larger disk diameters. The seed laser is then synchronised with a chirped amplifier system (CPA), described fully in the femtosecond laser system in section 3.1.7.

3.1.5. Picosecond laser system

Generation of the laser pulses in the picosecond time regime was achieved using a Trumpf (TruMicro 550) laser, which uses thin disk pulse generation technology. Pulses are generated at the fundamental wavelength of 1030 nm, with harmonic wavelength output available at 515 and 343 nm. The overall laser package consist of a pump module, a seed laser, a disk amplifier, external modulator and collimator. The technical specifications of the laser is given in Table 5.
Table 5 Technical specifications for the Trumpf picosecond laser system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fundamental wavelength</td>
<td>1030</td>
<td>nm</td>
</tr>
<tr>
<td>Pulse Duration</td>
<td>10</td>
<td>ps</td>
</tr>
<tr>
<td>Max Power Output</td>
<td>50</td>
<td>W</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>Single shot – 400</td>
<td>kHz</td>
</tr>
<tr>
<td>Spatial Mode</td>
<td>$TE_{M_{00}} (M^2 &lt; 1.2)$</td>
<td></td>
</tr>
<tr>
<td>Second harmonic generation</td>
<td>515 (Efficiency ≈ 50 %)</td>
<td>nm</td>
</tr>
<tr>
<td>Third harmonic generation</td>
<td>343 (Efficiency ≈ 15 %)</td>
<td>nm</td>
</tr>
</tbody>
</table>

The general setup consists of the output laser beam at the fundamental wavelength of 1030 nm. Flip mirrors are used to direct the beam to the relevant harmonic generation box if necessary. Beam steering mirrors then direct the beam to the galvanometer (Scanlab) and F-Theta lens (103 mm). In the case of 1030 nm picosecond pulses, a telescopic beam expander is used to increase the size of the laser beam. The optical setup of the picosecond laser is shown in Figure 3.4.
Table 6 shows the system specifications and optical setup used for each of the laser wavelengths, for ITO thin film patterning.
Table 6  Range of laser parameters for the picosecond laser used for ITO thin film patterning

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Pulse Duration (ps)</th>
<th>Repetition Rate used (kHz)</th>
<th>Raw Beam Output (mm)</th>
<th>Beam Expansion Factor</th>
<th>Aperture Size (mm)</th>
<th>Focal Length (mm)</th>
<th>NA</th>
<th>Focussed Spot radius (μm)</th>
<th>Fluence Range (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>343</td>
<td>&lt;10</td>
<td>10</td>
<td>3</td>
<td>2.5</td>
<td>5 – 8</td>
<td>103</td>
<td>0.009 – 0.039</td>
<td>6.5 – 22.7</td>
<td>0.4 – 4.0</td>
</tr>
<tr>
<td>515</td>
<td>&lt;10</td>
<td>10</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>103</td>
<td>0.026</td>
<td>22.7</td>
<td>0.70 – 3.63</td>
</tr>
<tr>
<td>1030</td>
<td>&lt;10</td>
<td>10</td>
<td>3</td>
<td>5.5</td>
<td>8</td>
<td>163</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.1.6. Femtosecond pulse generation

The generation of ultrafast laser pulses is controlled by a technique known as mode locking. Mode locking occurs when the phase of adjacent modes are in phase relative to each other. In this case, the emission of the pulse energy is in a single pulse with a period T. An active medium is also required, with a sufficiently broad bandwidth and high pump intensity. In many ultrashort lasers, and the femtosecond laser used in this study, this active medium is Yb:KYW crystal. The active medium is placed in Fabry – Perot cavity, where irradiation of the crystal by a diode laser takes place, resulting in population inversion in the crystal. Amplification of the laser pulse is necessary, in order to achieve greater laser pulse energies. The optimal way to achieve this uses a pair of reflective diffraction gratings. This is known as chirped pulse amplification (CPA). Firstly, the femtosecond laser pulse is temporally stretched up to $10^4$ times, which reduces the intensity of laser pulse. The low intensity pulse can now be amplified. Figure 3.5 shows the pulse stretching and compression using for the generation of femtosecond pulses, using diffractive grating pairs [161].
After the pulse is stretched, the pulse is put through a Pockel cell. The Pockels cell switches the stretched pulse in and out of amplification. The regenerative amplification technique is then used for amplification of the pulse. The pulse is kept in the resonator until the available energy in the amplifier cell is extracted. After exiting the amplifier, the stretched, high intensity laser pulse is then compressed, using a pair of diffractive gratings, using the reverse process to the pulse stretching gratings.

3.1.7. Femtosecond laser system

The femtosecond laser used in this study (Amplitude Systems S- Pulse HP) was a diode pumped ultra-fast solid state laser, with a Ytterbium doped laser medium. The system consists of a laser head, which contains the femtosecond oscillator, regenerative amplifier, and a pulse picker. The laser head consists of an oscillator, a laser diode to pump the crystal medium, followed by optics for pulse stretching and compression, then pulse amplification and modulation. The laser oscillator head emits a weakly powered pulse (≈ 20 nJ), 250 femtosecond pulse, with a repetition rate of 80 MHz, at a wavelength of 1030 nm. After emission from the femtosecond oscillator head, the pulse goes through a number of stages, as seen Figure 3.6.
The technical specifications of the femtosecond laser used in this study are shown in Table 7.

Table 7: Technical specifications for the Amplitude systems femtosecond laser system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fundamental wavelength</td>
<td>1030</td>
<td>nm</td>
</tr>
<tr>
<td>Pulse Duration</td>
<td>500</td>
<td>fs</td>
</tr>
<tr>
<td>Max Power Output</td>
<td>0.004 – 4</td>
<td>W</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>0.001 – 100</td>
<td>kHz</td>
</tr>
<tr>
<td>Spatial Mode</td>
<td>$TEM_{00}$ ($M^2 &lt; 1.2$)</td>
<td></td>
</tr>
<tr>
<td>Second harmonic generation</td>
<td>515 (Efficiency ≈ 50 %)</td>
<td>nm</td>
</tr>
<tr>
<td>Third harmonic generation</td>
<td>343 (Efficiency ≈ 30 %)</td>
<td>nm</td>
</tr>
</tbody>
</table>

All of the laser used in this study convert the original IR output light to lower wavelengths, using a process known as high harmonic generation. In this method, the laser pulse passes through a harmonic crystal. These consists of a lithium triborate crystal for second harmonic generation (515/532 nm), and barium borate for third harmonic generation (343/355 nm). High harmonic generation is a non-linear process where the laser pulse is converted into an integer multiple of its frequency. The higher frequency occurs when two photons are combined in the crystal, doubling the frequency, and therefore halving the wavelength. Frequency tripling can then occur when the green...
photon is combined with another IR photon, resulting in the output of a UV photon. This combining of photons results in a lowering of the overall efficiency of the output power. At green laser output, the overall power lower drops to ≈ 50 %, and at the UV laser output, the efficient drops to ≈ 33 %.

Femtosecond laser pulses with a 500 fs pulse duration were generated at a fundamental wavelength of 1030 nm. The interface box contains the THG and SHG for the generation of the 515 and 343 nm wavelengths. The optical layout of the harmonic box is shown in Figure 3.7. Table 7 shows the optical properties of the laser system.

![Fig. 3.7 Femtosecond laser system, consisting of the laser head and interface box, along with the optical layout for the generation of 343 and 515 nm laser pulses](image)

The laser power is controlled through an external attenuator, placed before the harmonic generation box. If 343 or 515 nm laser wavelengths are required, the orientation of the THG and SHG crystals must be optimised. This is achieved by placing a power meter at the harmonic box exit aperture, and adjusting the fine screws on the THG and SHG
crystals, until maximum power is achieved at the desired wavelength. Laser processing of the thin film samples was achieved using laser marking software Winlase, described earlier. The position of the samples was controlled using an XYZ Aerotech stage. The optical properties of each wavelength used for thin film laser patterning is shown in Table 8.

3.1.8. Laser Power and pulse energy control

Control of the laser power on all the laser systems, was achieved through an external attenuator setup. This has the advantage of allowing the consistent laser cavity conditions when varying the laser power. In the case of the nanosecond laser sources, the diode current can be maintained at a consistent level, limiting pulse-pulse instabilities. The power used was measured at the sample workpiece, after the galvanometer scanning system, this allows the various energy losses to be taken into account. The power, in Watts (W) was measured using a thermal head (Ophir).

The laser pulse energy $E_p$, for a single pulse can then be found, by using the measured laser power $P$, and the known laser repetition rate $Q$.

$$E_p = \frac{P}{Q}$$ (33)
3.1.9. Laser Spatial Mode

All of the laser sources used in this study operate in $TE_{M00}$ mode. This spatial distribution is known as a Gaussian spatial distribution. Laser modes are the standing wave solutions to the propagation mode of electromagnetic waves in the laser cavity. The irradiance distribution in the $TE_{M00}$ Gaussian mode is given a radially symmetric distribution which is given in equation (1).

![Figure 3.8 Normalised laser Gaussian mode showing the $1/e^2$ beam diameter, given by equation (1)](image)

In this spatial intensity distribution, 86.5\% of the pulse energy is contained in the $1/e^2$ diameter. This leads to the definition of the laser spot radius $\omega_0$, which is the radius at which the laser drops to $1/e^2$ of its peak intensity.

3.1.10. Laser spot radius and spot propagation

The optical delivery of the laser sources used in this study, are in a direct write configuration. This consists of a galvanometer scanning system and an F-Theta telecentric lens, which focus the laser pulse to the material surface. An approximate estimation of the spot radius at the focal point of a lens $\omega_0$ can be solved using geometric optics is given by equation (2). A more accurate calculation of $\omega_0$ can be found by relating the crater diameter in a material $D$, to the laser pulse energy $E_p$ through [97]

$$D^2 = 2\omega_0^2 \ln\left(\frac{\phi_0}{\phi_{th}}\right)$$  \hspace{1cm} (34)
Plotting $D^2$ versus the natural log of $E_p$ results in a typically straight line linear graph. The spot radius is then given by $\omega_0 = \sqrt{m/2}$, where $m$ is the slope of the graph.

3.2. Laser Ablation

In this section the laser ablation technical requirements are described, including the definition of the laser fluence, the laser threshold fluence and other key laser ablation parameters.

3.2.1. Laser Fluence

Integrating the applied pulse energy over the laser spot radius, leads to the definition of the peak applied laser fluence, an energy density, measured in $J/cm^2$.

$$\phi_0 = \frac{2E_p}{\pi\omega_0^2} \quad (35)$$

3.2.2. Laser Threshold Fluence

As the peak applied fluence is decreased, the minimum applied fluence required to visibly damage the surface, is generally referred to as the damage threshold fluence. This minimum energy density is typically found by plotting $D^2$ versus the natural log of the fluence $\ln(\phi_0)$, and extrapolating the curve to 0. The relationship between the applied fluence, the crater diameter and threshold fluence can be seen for various normalised applied fluences and threshold fluences, in Figure 3.9.
3.2.3. Threshold fluence using a tilted plane

Typically, the threshold fluence is measured at the focal point of the lens, at a fixed $\omega_0$. However in certain cases, the threshold fluence has been known to vary over the applied $\omega_0$. In order to quickly test the dependence of $\phi_{th}$ on the applied $\omega_0$, a tilted plane threshold method (developed at M-Solv lasers) was investigated in this study.

Figure 3.9 Applied fluence versus position for three normalised fluences, showing the respective crater diameters, for a normalised threshold fluence = 1

![Figure 3.9](image)

Figure 3.10 General schematic of the principal behind the tilted plane laser process
In this method, a tilted plane with a 1:10 vertical gradient was placed centred at the focal point of the lens. Scanning resolved craters along this gradient allows the focal spot size to be varied along the plane. Using the known gradient, the horizontal distance along the sample can be related to a vertical de-focus from the focal point. Using equation (3), the spot radius at this point $\omega(z)$ can be found at the vertical de-focus point. This can be related to the threshold fluence through

$$\phi_{th}(z) = \frac{\phi_0}{\exp(D^2/2\omega(z)^2)}$$

(36)

This threshold fluence can then be averaged over a range of applied fluences. This allows a whole range of spot radii to be tested, at a fixed numerical aperture. Figure 3.11 shows the relationship between the scanned ablated craters and the change in spot radius with $z$ position, for a tilted plane system.

---

Figure 3.11 (a) Relationship between the horizontal distance between craters and the vertical de-focus (b) Change in normalised fluence versus focal position for a 0.33 NA system
3.2.4. Overlap of laser pulses

Laser pulse overlap can be described either in terms of an overlap percentage, or in shots per area (SPA). SPA was chosen as a clearer method for describing laser pulse overlaps, as percentage overlap at high SPA’s is linear. The pulse overlap is related to the galvanometer scanning speed \( s \), the laser repetition rate of the laser \( Q_l \) and laser spot diameter \( D_s \) in the following way

\[
\text{overlap} = \frac{D_s - \frac{s}{Q_l}}{D_s} \times 100 \%
\] (37)

Figure 3.12 shows a visual representation of the relationship between the shots per area and the overlap.

![Figure 3.12 Relationship between the laser post overlap and shots per area](image)

3.3. Material Characterisation and Plasma Imaging

3.3.1. Atomic Force Microscopy

Atomic Force Microscopy (AFM) (Agilent 5500) was used to determine the film grain structure, film thickness and the morphology of the laser patterned features. The general technique behind atomic force microscopy is shown in Figure 3.13. The basic operation...
of AFM consists of measuring the force between the probe and the sample surface. The main components are the AFM probe, laser source and photodiode. The AFM tip is typically made from silicon nitride, which is generally a 3-6 μm pyramid with a tip radius of 7-20 nm [162]. The vertical and lateral deflection of the cantilever is measured by reflecting a laser beam off the cantilever, which is incident on a four-segment position sensing detector. The position of the tip on the surface is controlled using a motorised tip approach and piezo ceramic materials. This type of material expands or contracts under the influence of a voltage gradient. The force of the probe on the sample is regulated using feedback loops, which control in the probe force in real time. The feedback loop controls the height of the probe, the optical lever and the cantilever, along with keeping a consistent voltage applied to the cantilever to keep the deflection consistent.

A silicon nitride cantilever (Nanosensers PPP-Contr, resonance frequency 13 kHz, tip radius < 7 nm, force constant ~0.2 N/m) was used in contact mode with a scan speed of 1 line/s. Feedback gains in the range of 1-5 % were used. The exact setting of the probe position and feedback gains was varied, depending on the sample and scan size. Inter-atomic forces between the tip and surface induce a deflection in the cantilever. The

Figure 3.13 General schematic and principle for atomic force microscopy
reflection of a laser focussed onto the cantilever is monitored by a position sensitive photodiode. The deflection of the tip as the cantilever is moved across the surface, can then be used to generate a three dimensional topographical image. Contact AFM was chosen over other imaging methods, such as scanning electron microscopy (SEM), which would require deposition of a gold layer, which may obscure surface features on the very thin ITO film.

3.3.2. Optical transmittance and reflectance

The optical properties of the film was determined using a UV-VIS spectrometer, where the film transmission and reflectivity could be determined. The wavelength range was 200 - 1100 nm. The absorption coefficient was determined from the Beer-Lambert law given by equation (6), leading to an absorption coefficient

The absorption coefficient was determined from the Beer-Lambert law,

\[
\alpha(\lambda) = \left(-\frac{1}{d}\ln\left[T(\lambda)/\{(1 - R'(\lambda))(1 - R(\lambda))\}\right]\right)
\]  

(38)

where \(T(\lambda)\) is the measured transmission, \(R(\lambda)\) is the measured reflectivity of the air/ITO interface, \(R'(\lambda)\) is the estimated reflectivity at the ITO/glass interface, and \(d\) is the film thickness. The reflectivity between ITO on glass interface is estimated using the refractive indices of glass [163] and ITO [164], with the reflectivity given by the equation \(R'(\lambda) = \left[(n_{ITO} - n_g)/(n_{ITO} + n_g)\right]^2\). This results in ITO/glass interface reflectivity’s of 0.045, 0.030, 0.011, and 0.005 for wavelengths of 266, 355, 532 and 1064 nm, respectively. The accuracy of transmission values are ± 0.006.

3.4. Real time plasma imaging

The plasma imaging setup used a iCCD camera (Andor iStar) to image the expanding laser plasma, at fixed times after laser irradiation. Plasma imaging requires two important characteristics. It must be possible to generate a single laser pulse, which has a fixed output time relative to some measurable signal. This signal must then be used to trigger both the laser pulse and the camera. This signal gives the initial \(t_0\) time, on which all of
timing delays are based. The CCD camera used as an adjustable built-in delay, which can be used to image the plasma at fixed times relative to the incident laser pulse. Figure 3.14 shows the general schematic for the plasma imaging setup used.

![Figure 3.14 Plasma imaging schematic. The plasma is placed at the focal point of the 10 x objective, and the incident light is brought to CCD camera](image)

The line of vision extended by the camera was orthogonal to the plane of incidence of formed by the incident laser. A microscope objective (Nikon, 10x, f=200 mm, NA = 0.28) is used to capture the light and image it to the CCD camera. A zoom telescope (Navitar 6000 zoom) is used to control the size of image field. The zoom was varied depending on the overall size of the emitted plasma. Using the relationship between the pixel count and the angular spread of the camera, the plume dimensions and plume velocity can be estimated. The dimensions of the plasma were calibrated using a target sheet, which had a fixed concentric circular rings of 0.5 mm in diameter. Once the pixel size on the image is known, the height of the plasma can be translated to any height in millimetres. The velocity of the plasma can then be estimated simply using the formula \( v_p = \frac{h_p}{t_p} \), where \( v_p \) is the plasma velocity, \( h_p \) is the plasma height and \( t_p \) is the time of the plasma evolution.

### 3.4.1. Plasma Imaging using nanosecond laser pulses

In order to image the laser plasma, the generation of the single laser pulse, with a known and fixed flight time to the material is required. Using internal trigger methods, such as
typically used with Galvanometer optics, results in a variable time between the rising edge of the external gate, and the output laser pulse, which is sub-optimal for timed imaging experiments as they require precise time. In order to overcome this, the laser was externally gated and triggered, which allows a fixed time between the gate signal and the output laser pulse. In order to achieve this, a custom fixed pin system was developed and implemented on the HIPPO laser system. Pin 17 and 21 where controlled using two separate digital pulse generators. On Pin 17, the gate was controlled using a TTL, with a length of 333 µs. The gate signal is used to control the rise and fall of the diode current. The rising edge of the gate signal initiates the rise of the diode current, and a fixed suppression time after the gate signal. The rising edge of this gate signal was then used to trigger the second signal generator, which emitted a 30 KHz TTL signal, which was sent to Pin 21, the Q-switch trigger, on the external laser controller. The Q-switch trigger controls the emission of laser energy from the diode. The relationship between the gate, trigger signal and laser output can be seen Figure 3.15

![Figure 3.15 Relationship between the external gate signal, external trigger signal and the laser optical output for the HIPPO nanosecond laser system (Spectra Physics HIPPO operation manual)](image)

The suppression time between the falling edge of the gate and the optical output, can be varied in the laser software. The suppression time was set to the default 260 µs. The standby current of the diode could also be varied. This was set at 18 A, a level which was found to suppress the emission of large intensity first laser pulses. The external gate and external repetition rate trigger signals were set using two separate signal generators (Stanford Research). In order to synchronise the whole timing process, the rising edge of
the external gate signal was defined as $t_0$, the absolute zero of the timing. The laser output, camera and were all triggered off this signal. In order to ensure synchronisation between the external gate and repetition rate trigger signal, the output of the signal square gate was used as the external trigger for the repetition rate signal. The external gate signal was then used to trigger the CCD camera, and the delay on the camera could be set to synchronise with the arrival of the nanosecond pulse. Figure 3.16 shows a block schematic of the synchronisation of the plasma imaging nanosecond setup.

![Nanosecond Plasma Imaging: Timing and Synchronisation](image)

Figure 3.16 Timing and synchronization of nanosecond laser pulses for plasma imaging

The time between the trigger signal and the laser pulse emission was measured using a photodiode. In order to ensure only a signal pulse is picked, the length of the gate signal was varied, and set to 333 µs, the time where only one pulse was detected on the photodiode. Figure 3.17 shows the relationship between the externally generated gate and Q-switched gate signal, along with the single laser pulse detected.
The time between the rising edge of the external gate and the laser pulse optical output was then determined to be 304.86 µs.

3.4.2. Plasma Imaging using femtosecond laser pulses

In the femtosecond time regime, the pulse picker signal was used to trigger the CCD camera. In order to understand the relationship between the oscillator pulse, pulse picker pulse, and laser output pulse, the control signals were monitored by using an oscilloscope.
Low power oscillator pulses are generated every 20 ns. The amplification of the oscillator pulse is controlled by the repetition rate, set in the computer software. The rising edge of the amplifier pulse triggers the pulse picker pulse. The duration of the pulse picker pulse is approximately 1000 ns, as seen in the yellow trace in Figure 3.18. The relationship between the rising edge of pulse picker and the output of a laser pulse, is then fixed at 1.036 µs.

Using this fixed delay, the camera can also be triggered off the rising edge of the pulse picker pulse, and using the in-built delay settings in the camera software, camera and pulse synchronisation can take place. The generation of a single femtosecond pulse is achieved through the use of an external pulse generator (Stanford Research Systems). The external pulse generator is used to gate a single pulse picker pulse, which then emits a single laser output pulse. A 5V TTL pulse with a duration of 1000 ns was used to gate the pulse picker pulse.
3.5. Thin film materials

Here a description is give on the thin film material used in this study, including the fabrication conditions and material constants.

3.5.1. ITO on dielectric glass

The polycrystalline ITO thin film samples were deposited on chemically strengthened Gorilla glass (10X-FS Corning, 0.5 mm), by DC sputtering (Aimcore, Taiwan). The DC sputtering takes place in a vertical configuration, with $In_2O_3$ and $SnO_2$ targets prepared from powder forms. The supplied film material constants give a sheet resistance of $80\, \Omega/\square$, a resistivity of $2.8 \times 10^4 \, \Omega cm$, with an estimated carrier concentration of $\sim 3.2 \times 10^{20} \, cm^{-3}$. The main film thickness used was verified experimentally to be 20 nm, with a grain size of 20 - 30 nm. The sheet resistance, measured using a standard 4 point probe, typically varies by 10 % across a single deposited sheet, principally due to changes in deposition temperature, thickness and carrier concentration.

3.5.2. ITO on PET

ITO thin films were also deposited on PET polymer substrates, with a film thickness of 20 nm, and a substrate thickness of 0.3 mm.

3.6. Finite Element Thermal Simulations: COMSOL

The finite element method is a numerical method for solving complicated problems in maths and science. Finite element analysis allows is useful for solving problems where analytical solutions are not available. The finite element simulations solve the differential equation at the boundaries of the mesh system implemented in the program. The COMSOL 5.1 interface is divided into a number of sections, which are described below.

- **Parameters:** In this section, the non-variable parameters are defined, which stay constant during the simulation. These include pulse energy, laser spot radius, laser fluence, reflectivity, absorption coefficient, and the laser pulse duration.
• **Variables:** Here the variables of the simulation are defined. Variables are defined as anything which varies with the dependents of the simulation, in this lattice temperature (T) and time (t).

• **Geometry:** Here the geometry of the simulation is defined. In this case, two rectangles are created, representing the film and substrate.

• **Materials:** The material parameters are defined in this section, for both the film and substrate. This includes the thermal conductivity, heat capacity at constant pressure, and the density. The Young’s modulus, Poisson’s Ratio, and the coefficient of thermal expansion are also defined here, in the case of the thermal stress model.

• **Heat Transfer Module:** Here, the 2-D heat equation is solved with the respect to the parameters and variables defined. A heat source is defined in this section, which calls the variable \( I(x, y, t) \) from the variable section.

• **Mesh:** In this section, the mesh of the geometry is defined. The mesh was set as a free triangular mesh, and the size of the mesh set to 10 nm.

• **Study Sequence:** Here, the model sequence is generated. The time step variables are set, typically starting at 0 ns, to 50 ns, in 1 ns steps.

The geometry of the simulation is set into two rectangles, representing the thin film and substrate, with dimensions of 50 μm X 20 nm for the film, and 50 μm X 1 μm for the substrate. The boundary conditions of the edges are set to free. At the In order to solve differential equations, according to the input parameters, discretization of the geometry into a mesh must take place. The mesh is defined as an equivalent system of smaller bodies, interconnected at points and/or boundary lines. The size of mesh determines the complexity of the solution, and determines the accuracy of the intended solution. A direct relationship is seen between the mesh size, and the time taken for the solution to converge to a stable solution. The mesh size was set in a triangular format, with minimum dimensions on the y direction of 0.1 nm. As the y direction in the film is the minimal critical length, the x mesh size is not as sensitive to the mesh size. Therefore in order to save on computing time, the x mesh size is scaled to be larger than the y mesh size, by a factor of 50, giving an x mesh size of 25 nm. The optimum mesh size was determined by examining the mesh convergence. In this way, the mesh size was decreased while
examining the parameters under observation. Once a steady solution was reached, the mesh size was kept at this optimum value.

The general flow of the finite element model takes place in three stages.

- **Pre-processing**

Here the geometric entities of the model are defined, including properties such as length and size. The relevant material properties are also defined. The element connectivity’s (mesh) and boundary problems are defined.

- **Solution**

The primary field variable are computed using all the input parameters and material properties.

- **Post-processing**

In the post-processing section, the data can be sorted and analysed. Typically, for the heat solutions, the temperature distributions can be extracted from the solution, along any directions, typically in the radial and depth directions, corresponding to the film temperature, and temperature into the substrate.

### 3.6.1. ITO on glass nanosecond thermal heating simulation

The heat equation given by (9) was solved using a time dependent solver. The laser source term is given by (11). The solution to the heat equations at solved in 0.1 ns steps, ending at a total time of 50 ns. The heat equation is solved with the initial conditions \((r, t) = T_a\), at \(t = 0, T_a = 300 \, K\), the ambient temperature. The laser and material properties of the film and substrate are shown in Table 9. The material properties are assumed to be temperature independent, unless otherwise shown. The absorption coefficient is calculated experimentally, with the results presented in 4.1.
Table 9 Laser and material properties used in ITO on glass heating simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Wavelength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Lambda )</td>
<td></td>
<td>266 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>355 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1064 nm</td>
</tr>
<tr>
<td>Pulse Duration FWHM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tau_p )</td>
<td></td>
<td>266 nm 8.6 ns</td>
</tr>
<tr>
<td></td>
<td></td>
<td>355 nm 20 ns</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532 nm 9 ns</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1064 nm 9.2 ns</td>
</tr>
<tr>
<td>Reflectivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R )</td>
<td>ITO (355 nm)</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>ITO (266 nm)</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>ITO (532 nm)</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>ITO (1064 nm)</td>
<td>0.05</td>
</tr>
<tr>
<td>Absorption Coefficient</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha )</td>
<td>ITO (355nm)</td>
<td>( 4 \times 10^6 , m^{-1} )</td>
</tr>
<tr>
<td></td>
<td>ITO (266 nm)</td>
<td>( 3.9 \times 10^7 , m^{-1} )</td>
</tr>
<tr>
<td></td>
<td>ITO (532 nm)</td>
<td>( 7.9 \times 10^8 , m^{-1} )</td>
</tr>
<tr>
<td></td>
<td>ITO (1064 nm)</td>
<td>( 1.1 \times 10^9 , m^{-1} )</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td>( 1 \times 10^4 , m^{-1} ) [165]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \kappa )</td>
<td>ITO</td>
<td>10 W/mK [166]</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td>0.9 W/mK [167]</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \rho )</td>
<td>ITO</td>
<td>7120 kg/m(^3) [168]</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td>2220 kg/m(^3) [167]</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_\rho )</td>
<td>ITO</td>
<td>340 J/kg K [169]</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td>( 708.11 + 0.29917 \times T ) J/kg K [167]</td>
</tr>
<tr>
<td>Melting Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T_m )</td>
<td>ITO</td>
<td>1900 K [170]</td>
</tr>
<tr>
<td>Vaporisation Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T_v )</td>
<td>ITO</td>
<td>3000 K</td>
</tr>
<tr>
<td>Latent Heat of Fusion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( L_f )</td>
<td>ITO</td>
<td>( 5 \times 10^5 ) J/kg</td>
</tr>
<tr>
<td>Latent Heat of Vaporisation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( L_v )</td>
<td>ITO</td>
<td>( 5 \times 10^6 ) J/kg</td>
</tr>
</tbody>
</table>
In the literature no data is available on the vaporisation point, latent heat of melting, or latent heat of vaporisation of ITO. Therefore in this study they were approximated to be 3000 K, $5 \times 10^5 \, J/kg$, and $5 \times 10^6 \, J/kg$ which are reasonable estimates considering the values of similar metals and semiconductors [171].

The nanosecond lasers used in this study have different pulse durations, depending on the wavelength used. Figure 3.19 shows the change in the temporal Gaussian intensity profile for the nanosecond lasers used. The 355 nm laser source has a longer pulse duration at 20 ns full width half maximum.

![Normalized laser temporal profile for the ns pulses used as wavelengths of 266, 355, 532 and 1064 nm](image)

Figure 3.19 Normalised laser temporal profile for the ns pulses used as wavelengths of 266, 355, 532 and 1064 nm

The material properties used are in general accurate, however a number of assumptions are made. The ITO material properties are assumed to be temperature independent. This is because no reliable data was found in the literature which describes how these parameters react under increasing temperature. The phase change for melting and vaporisation in the film and substrate is approximated using Gaussian functions, shown in (10), to simulate the increase in material heat capacity, as the material overcomes the added latent heat of phase change. Figure 3.20 shows the estimated change in heat capacities for the ITO film and glass substrate with increasing temperature.
3.6.2. ITO on PET thermal heating and strain/stress simulation

When materials experience heating, material expansion can take place, which can lead to an associated strain and stress in the material. The thermal stress module of COMSOL allows the effect of increasing temperature, material expansion and therefore stress/strain at an interface to be simulated. The material displacement, strain and stress are solved using (23) - (27). The temperature used to calculate the thermal expansion is found by solving equation (9) simultaneously. The material inputs in to the model are the same as Table 9, however in order to calculate the strain and stress, the mechanical properties of the thin film and substrate materials must be estimated, as seen in Table 10.

Figure 3.20 (a) Simulated change in heat capacity in the ITO film as a function of temperature (b) Simulated change in heat capacity in the glass substrate as a function of temperature
Table 10 COMSOL coefficients for thin film and substrate stress/strain simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Coefficient</td>
<td>ITO (355nm)</td>
<td>$3.3 \times 10^6 \text{ m}^{-1}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>PET (355 nm)</td>
<td>$1 \times 10^6 \text{ m}^{-1}$ [171]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>ITO</td>
<td>$10 \text{ W/m K}$ [166]</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>PET</td>
<td>$0.15 \text{ W/m K}$ [155]</td>
</tr>
<tr>
<td>Density</td>
<td>ITO</td>
<td>$7120 \text{ kg/m}^3$ [168]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>PET</td>
<td>$1450 \text{ kg/m}^3$ [171]</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>ITO</td>
<td>$340 \text{ J/kg K}$ [169]</td>
</tr>
<tr>
<td>$c_\rho$</td>
<td>PET</td>
<td>$2100 \text{ J/kg K}$ [90]</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>ITO</td>
<td>$190 \text{ GPa}$ [172]</td>
</tr>
<tr>
<td>$E$</td>
<td>PET</td>
<td>$0.6 \text{ GPa}$ [173]</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>ITO</td>
<td>0.35 [172]</td>
</tr>
<tr>
<td>$\nu$</td>
<td>PET</td>
<td>0.34 [174]</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td>ITO</td>
<td>$5 \times 10^{-6} \text{ K}^{-1}$ [175]</td>
</tr>
<tr>
<td>$\alpha_T$</td>
<td>PET</td>
<td>$70 \times 10^{-6} \text{ K}^{-1}$ [176]</td>
</tr>
</tbody>
</table>

The model is run with the same initial conditions and settings, as described in section 3.6.1. The output of the model gives the temperature of the film and substrate, at all the time steps. The strain and stress is monitored in terms of the strain and stress tensors described in equations (24) and (26).

3.6.3. Two temperature model

The two temperature model can be used to estimate the temperature of the electronic and lattice subsystem, for both picosecond and femtosecond pulses. This is achieved in COMSOL by solving equations (14) - (18). The source term is estimated using (11). Table 11 shows the parameters used for the ITO film in the two temperature model. The estimated optical properties such as material reflectivity and absorption coefficient are taken from Table 9.
Table 11 Optical and material constants used for TTM simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number density of electrons</td>
<td>( n_e )</td>
<td>( 10^{21} )</td>
<td>( cm^{-3} )</td>
</tr>
<tr>
<td>Boltzmann’s constant</td>
<td>( k_B )</td>
<td>( 1.38 \times 10^{-23} )</td>
<td>( m^2 kg s^{-2} K^{-1} )</td>
</tr>
<tr>
<td>Fermi Energy</td>
<td></td>
<td>3.3 [177]</td>
<td></td>
</tr>
<tr>
<td>Lattice Heat Capacity</td>
<td>( c_p )</td>
<td>( 2.4 \times 10^6 ) [169]</td>
<td>( J m^{-3} K^{-1} )</td>
</tr>
<tr>
<td>Mass of the electron</td>
<td>( m_e )</td>
<td>( 9.109 \times 10^{-31} )</td>
<td>kg</td>
</tr>
<tr>
<td>Effective mass of the electron</td>
<td>( m_e^* )</td>
<td>0.35( m_e ) [177]</td>
<td>kg</td>
</tr>
<tr>
<td>Speed of sound</td>
<td>( C_s )</td>
<td>340.49</td>
<td>m/s</td>
</tr>
<tr>
<td>Electron scattering time</td>
<td></td>
<td>6 \times 10^{-15} [178]</td>
<td>s</td>
</tr>
<tr>
<td>Speed of Sound</td>
<td>( c_s )</td>
<td>5.56 \times 10^3</td>
<td>m/s</td>
</tr>
<tr>
<td>Pulse Duration</td>
<td>( \tau_p )</td>
<td>500 fs – 10 ps</td>
<td>-</td>
</tr>
</tbody>
</table>

Due to the lack of data on the bulk modulus of ITO, the value used in the simulation was simplified to that used for gold films in similar TTM models [179]. The electron and lattice temperature can then be examined for a number of varying parameters, such as pulse duration, wavelength and applied fluence. The electron temperature is then applied to solve the ultrafast lattice deformation equations, given as equation (28).

3.7. Summary

In this chapter, an in-depth summary of the materials, equipment and methods was presented. The laser systems and optical setups in the three main pulse duration regions were described, along with their application to thin film processing. The real time plasma visualisation techniques were also shown, along with the timing and synchronisation required. The experimental methods and surface analysis techniques were also described.
Chapter 4

4. Laser- thin film interaction

Nanosecond laser and ultrashort ablation of ITO thin films has been discussed previously in the literature, mainly concentrating on selective removal of the film from the substrate. Generally, ITO film removal has been investigated for films much thicker than used in this study, typically in the range of 100 - 500 nm [48, 152, 154, 157, 165, 180-182]. However, the exact removal mechanisms of the ITO thin film and damage mechanisms to the underlying substrate, are still not fully understood. This chapter aims to undertake a detailed study into the interaction of laser pulses various properties and the ITO thin film, through a number of experimental methods.

The key objectives of this chapter is as follows

- To analyse the laser threshold fluence of the ITO thin film, and determine its dependence on the applied laser wavelength, pulse duration, film thickness and other irradiation conditions

- To determine the thin film removal properties across a range of laser wavelengths, with consideration towards the choice of substrate material effect of the substrate material

- To determine how glass damage varies across the applied laser wavelength, and determine the absorption mechanisms which lead to glass damage

- To analyse the ejection of laser plasma in ambient conditions for both ITO on glass and ITO on PET, at nanosecond and ultrashort pulse durations
• To analyse the effect of laser pulse incubation and overlap, in terms of the film surface topography and film removal

4.1. ITO thin film surface analysis and ablation properties

The irradiation of ITO films was examined using nanosecond, picosecond and femtosecond laser pulses, using the laser systems described in 3.1. The interaction of the film with the laser was examined for both single shot and multi-pulse configurations. The surface topography of the craters was analysed using AFM.

4.1.1. Thin film surface and optical properties

The surface of the ITO thin film was examined using AFM, in order to determine the grain structure of the film. Figure 4.1 shows a 500 X 500 nm surface topography grain structure of the ITO film and glass substrate observed from the laser patterning features.

Figure 4.1 ITO surface morphology examined using AFM, showing the grain structure of the film. The grain size is 20 – 30 nm, with a surface roughness of 0.51 nm. The grain structure of the film is much more prominent
The grain size of the polycrystalline films were estimated to be approximately 20-30 nm. The $R_a$ surface roughness was calculated to be 0.51 nm. The estimated thickness of the ITO film was $20 \pm 1$ nm. The glass substrate has a much smoother amorphous grain structure. The grain structure observed for ITO on PET showed the same grain characteristics. However in this case, the film thickness was 30 nm.

The transmission and reflectivity of the ITO film was determined across a wavelength range from 200 – 1100 nm, using a UV-VIS spectrometer, described in section 3.3.2. This allowed the film reflectivity and absorption coefficient to be examined at the laser wavelengths used in this study. Figure 4.2 shows the measured transmission and reflectivity from the 20 nm ITO on glass sample.

![Figure 4.2 ITO film transmission and reflectivity as a function of wavelength for 20 nm ITO on glass](image)

In general, the transmittance increases with increasing wavelength, while the reflectivity decreases with increasing wavelength. Table 12 shows the measured film reflectivity, transmittance, and calculated absorption coefficient across the range of wavelength of interest in this study, calculated from (38).
Table 12 Relationship between the applied laser wavelength, and the measured film absorption coefficient

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>266</th>
<th>355</th>
<th>532</th>
<th>1064</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectivity</td>
<td>0.32</td>
<td>0.31</td>
<td>0.11</td>
<td>0.05</td>
</tr>
<tr>
<td>Absorption Coefficient ($m^{-1}$)</td>
<td>$3.9 \times 10^7$</td>
<td>$4 \times 10^6$</td>
<td>$7.9 \times 10^5$</td>
<td>$1.1 \times 10^6$</td>
</tr>
</tbody>
</table>

The highest absorption coefficient is seen at 266 nm, with a rapid decrease in absorption coefficient as the wavelength is increases to the IR. The values calculated for the absorption coefficient and reflectivity are consistent with values found for similar ITO films in the literature [21, 183, 184]. Minor variations in the values are seen, which is due to variations in the film due to fabrication conditions, thickness, doping percentage and electronic density.

4.1.2. Laser irradiation of ITO films on glass using nanosecond laser sources

When the energy density of the laser pulse on the surface of the film exceeds a certain threshold fluence, craters are formed on the film surface. The surface topography of these craters was examined for laser pulses across the range of wavelengths used. In this section, the pulse duration of the lasers was in the nanosecond time regime. The applied fluences were chosen in this section are selected in order to show the best selective removal of the film from the substrate. In general, as shown further on, the surface topography of the craters is highly dependent on the applied laser fluence. Figure 4.3 shows the ITO crater surfaces imaged using AFM, at wavelengths of 266, 355, 532 and 1064 nm.
The crater surface shows a dependence on the applied wavelength. The main difference is noted at 266 nm, where a number of differing surface features are observed. Firstly, selective removal of the film is examined in Figure 4.4, which shows the half cross sectional profile of ITO craters shown in Figure 4.3. In each case, the profile is taken at the centre point across the crater.
Figure 4.4 ITO crater topography for applied nanosecond laser pulses, at wavelengths of 266 (0.83 J/cm²), 355 nm (1.5 J/cm²), 532 nm (5 J/cm²) and 1064 nm (2.5 J/cm²). Blue region indicates the 20 nm film region, while the gray region indicates the glass region. Due to the different crater sizes, each profile is normalised so that crater begins at the same point.

Selective removal of the film with a totally depth of 20 nm is observed at 355 and 532 nm. The ripple crater floor structure observed at 1064 nm, which is shown further in Figure 4.5, results in a maximum crater depth in the region of 16-18 nm, however the overall profile is flat along the crater; this indicates that complete removal of the film has taken place. The period of these structures is 394 ± 5 nm. The total depth for the 266 nm pulse is 25 nm, indicating 5 nm of damage to the glass substrate. Selective removal of the film without glass damage at 266 nm was not observed.

The surface topography of the nanosecond craters can be segregated into two distinct visual groups. The visual removal is consistent at wavelengths of 355, 532 and 1064 nm, in contrast to a large visual change at 266 nm. These two groups from here are labelled in terms of their optical absorption properties as the direct band to band transition group for 266 nm, and non-direct band to band transition group at all other wavelengths. The ITO film has an estimated band gap of 3.8-4 eV band gap, only 266 nm laser pulses can excite an electron across the direct bad gap. Further in depth examinations were carried out on the crater edge and the crater floor. Figure 4.5 shows the crater edge after laser irradiation at the four applied wavelengths.
A distinctive re-solidified melt ridge is observed at wavelengths of 355, 532 and 1064 nm. The height of the ridge is in the region of 35-40 nm, with small variations noted with applied fluence and applied spot radius. A noticeable ripple structure is observed in the glass at 1064 nm. At 266 nm, the re-solidified crater ridge is different in both height and width, compared to all other applied wavelengths. The crater ridge itself is 5 nm in height, spread out over 2-3 μm. The ridge itself has a ripple structure in nature, connecting the crater and edge of the heat affected zone. Circular structures on the ridges are also visible, randomly distributed across around the crater. The crater floor was also examined at wavelengths of 266 and 355 nm, as seen in Figure 4.6.
The grain structure of the crater floor shows a variation between the two visually distinctive groups. At 355 nm, distinctive grains are observed on the crater floor, with a $R_a$ surface roughness is 0.53 nm, along the flat crater floor. The grain structure of the crater floor is similar to the grain structure of the film itself, however, the grains appear to be larger, with a grain size of 50 -100 nm. In the case of selective removal of the film at all of the non-direct band to band transition wavelengths, no re-deposition of ablated matter and nano-particles appears around the crater, at wavelengths. The crater floor at 266 nm shows re-deposited matter across the crater floor. The size of these particles ranges from 100-500 nm in size. The features crater floor for 266 nm is confirmed to be weakly adhered particles, as after cleaning the material surface with a mild alcohol solution, the particles can be removed. Overall, the crater formation is visually consistent at wavelengths of 355, 532 and 1064 nm, with major changes to the crater topography at a wavelength of 266 nm, in terms of the crater ridge and selective removal of the film from the substrate.

4.1.3. Dependence of the ITO on glass surface topography on applied spot radii

The effect of increasing laser spot radius on the crater surface topography was examined for 355 nm laser pulses. Crater were made using three different optical configurations, which resulted in different spot radii. The spot radius was varied by adjusting the aperture in the optical setup shown in Figure 3.3. Figure 4.7 shows the surface topography of the
selectively removed ITO film, for laser spot radii of 10.0, 16.1, and 25.9 µm. The applied fluence in each case is 1.5, 1 and 0.9 J/cm².

As the spot radius is increased, the surface topography changes terms of the re-solidified melt ridge. Ridge heights of 40 and 10 nm are observed for spot radii of 10 and 16.1 µm, with no significant ridge observed at a spot radii of 25.9 µm. Selective removal of the film from the substrate is observed at all the applied spot radii, when scaled to the appropriate applied fluence.

4.2. Ultrashort ITO on glass crater analysis

The ITO films were irradiated with laser pulses in the picosecond and femtosecond time regime, using the optical setups described in section 3.1.5 and 3.1.7. After laser irradiation, the surface was imaged using AFM. The surface topography of the craters
was examined in terms of selective removal of the film from the substrate, crater edge quality and nanoparticle composition.

4.2.1. Laser irradiation of ITO films using femtosecond laser pulses

Figure 4.8 shows the typical film surface topography at wavelengths of 343, 515 and 1030 nm, in femtosecond time regime. For these craters, the applied fluence is chosen to illustrate best selective removal of the film from the substrate. The cross sectional crater profile is also shown.

![AFM surface topography of ITO on glass craters, showing selective removal of the ITO film, at wavelength of 343 (0.8 J/cm²), 515 nm, (1.4 J/cm²) and 1030 nm (1.2 J/cm², fs). Selective removal is observed at all wavelengths, with significant re-deposited particles, and no observed melt ridge.](image)

In general, the craters are very similar across the range of wavelengths and pulse durations used. In all cases, re-deposited material is noted in the crater area, the film is selectively removed from the substrate, and a particle based ridge, as opposed to a melt based ridge, is also observed, with a height of 40-70 nm. However, a number of differing structures can be observed, depending on the applied fluence, wavelength and pulse duration. Firstly
in the femtosecond time regime, at 515 and 1030 nm, two regions are visible in the ablation area, an inner portion, where the film is selectively removed, and an outer portion where incomplete removal of the film is seen. The crater edge is examined further in Figure 4.9 across the range of femtosecond wavelengths used.

Figure 4.9 Crater edge for ITO on glass for laser pulses at (a) 343 nm fs, (b) 515 nm fs and (c) 1030 nm fs. A fragmented crater edge is clearly observed at 343 and 1030 nm. Two distinct ablation regions are observed at 515 nm.
In all cases, except at 515 nm, a fragmented and cracked crater edge is visible. Some of fragmented particles are large in nature, especially visible at 343 nm, with fragment sizes in the range 100 -200 nm. At 515 and 1030 nm in the fs time regime, the two separate ablation regions are clearly visible. In the case of 515 nm, the outer non-selective region is on the outer 6 µm region of crater, with a defined cut-off point between the two regions. A nanostructured area is visible at 1030 nm in the outer ablation region.

4.2.2. ITO on glass craters using picosecond laser pulses

The surface topography was also examined for picosecond laser pulses, at wavelengths of 343 and 1030 nm. In this case, the surface topography shows a dependence on the applied fluence. Figure 4.10 shows the surface topography of the ITO on glass craters after laser irradiation with 1030 nm picosecond pulses, with applied fluences of 0.6 J/cm², 1.1 J/cm² and 1.9 J/cm². The cross sectional crater profiles is also shown.

Figure 4.10 ITO on glass ablation craters using 1030 nm picosecond pulses at applied fluences of (a) 0.6 J/cm², (b) 1.1 J/cm², (c) 1.9 J/cm² (d) shows the cross sectional profile of the craters at the three applied fluences
The crater topography shows changes based on the applied fluence. At the lowest applied fluence of 0.6 J/cm², incomplete removal of the film from the substrate is seen, with only 10 nm of the 20 nm film being removed. The resulting crater floor is very rough, with extensive re-deposited nanoparticles in the ablation area. The crater edge shows significant cracking and fragmentation, with a maximum edge height of 8 nm. At an applied fluence of 1.1 J/cm², complete selective removal of the film takes place in the centre portion of the crater. Crater floor roughness can be observed at the crater edge, with smoother removal in the middle of the crater. The crater edge still shows evidence of cracking, however the ridge appears to be more particle based, with a height of 20 nm. At the highest applied fluence of 1.9 J/cm², no evidence of edge cracking can be seen, and no crater floor roughness is observed. The total depth at 1.9 J/cm² is 30 nm, indicating 10 nm of glass damage. Therefore, the “smooth” removal of the film at this fluence is actually accompanied by very minor damage of the glass substrate.

The surface topography as a function of applied fluence was also examined for 343 nm picosecond laser pulses, as seen in Figure 4.11. The three applied fluences shown are at 0.52, 0.87 and 1.43 J/cm², along with the cross sectional profile in each case.
Again the surface topography follows the same change in appearance as observed for 1030 nm. Incomplete removal of the film from the substrate is observed at the lowest applied fluence of 0.52 J/cm², with a total depth of 10-15 nm. The crater edge shows large re-deposited particles, with a height of 15 nm. The resulting crater floor shows significant roughness. Selective removal of the film from the substrate is observed at the next two fluences of 0.82 and 1.43 J/cm², with a crater edge height of 15 nm. Evidence of larger particles in region of 80 - 100 nm are scattered randomly around the crater area.

4.2.3. Re-deposition of nanoparticles after ultrashort laser irradiation

The crater floor was examined across the range of ultrashort laser pulses used. Re-deposited nanoparticles were observed at all the applied wavelengths and ultrashort pulse durations used. Figure 4.12 shows a section of the crater floor for the pulses used at picosecond and femtosecond pulse durations. The crater floor is examined in each case for craters shown in Figure 4.9, Figure 4.10, and Figure 4.11.
Figure 4.12 Crater floor showing deposited nanoparticles after laser irradiation for (a) 343 nm fs pulses, (b) 515 nm fs pulses, (c) 1030 nm fs pulses (d) 1030 nm ps pulses and (e) 343 nm ps pulses. The surface topography of all the crater floors are visually similar, except for 343 nm femtosecond. At this wavelength, the particles have re-solidified molten appearance.

Visually, the nanoparticles are very similar, with a triangular pointed appearance, except at 343 nm, where more spherical smoother nanoparticles are observed. The size of the
nanoparticles was examined across the range of wavelengths. Figure 4.13 shows the frequency distribution of re-deposited nanoparticle diameters for 343, 515 and 1030 nm femtosecond pulses, and 343 and 1030 nm picosecond pulses, for the surface topography profiles observed in Figure 4.12. The average nanoparticle was calculated from the data set. The error value is calculated as the standard error the data set.

![Graphs showing frequency distribution of nanoparticle diameters](image)

Figure 4.13 Frequency of nanoparticle diameter for applied femtosecond laser pulses at 343, 515 and 1030 nm, and picosecond laser pulses at 343 and 1030 nm. In general the average nanoparticle diameter increases with increasing wavelength.

In general, the size distribution of the nanoparticles is quite narrow for all the applied laser pulses. The average nanoparticles diameter for femtosecond pulses were 54.1 ± 2.2, 29.1 ± 1.2, and 19.2 ± 0.4, for wavelengths of 343, 515 and 1030 nm. The average nanoparticle diameter for ps pulses, was 28.3 ± 1 and 20.4 ± 1.2 nm at wavelengths of 343 and 1030 nm. Overall the nanoparticle re-deposition is consistent across all the wavelengths used, expect at 343 nm in the femtosecond pulse duration.
4.3. ITO on glass overlapped pulses

In order to create lines in the film, successive laser pulses must be overlapped. This overlap is typically measured in shots per area (SPA). The overlap is defined by the laser repetition rate and the scan speed of the galvanometer. The overlapped crater features could then be compared between nanosecond and femtosecond pulses. A wavelength of 355 nm was examined in the nanosecond time regime, and 1030 nm in the femtosecond time regime. Figure 4.14 shows the ITO film surface topography for pulses overlapped at SPA’s of 2, 5 and 15, along with the radial profile along the line. The applied fluence is 1.5 J/cm².

![Figure 4.14 355 nm nanosecond ITO on glass trench ablation, at SPA’s of 2, 5 and 15. The applied fluence in each case is 1.5 J/cm². Smoother removal is noted as the SPA is increased](image-url)

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Selective removal of the film from the substrate is observed, for all applied SPA’s. However, ripple-like structures are observed at the pulse overlap point, where the re-solidified melt flow results in a ridge. In the AFM images, the laser shots originate from the left of the image and scan towards the right hand side. The re-solidified ridge from the first pulse, shows little laser absorption, and is un-affected by the second pulse in the overlap. The size of the re-solidified ridge shows a direct dependence on the SPA. The height of re-solidified ridge decreases with increasing SPA. Changing the SPA from 1 – 15, results in ridge height decrease of 35 to 5 nm. Smoother removal of the film is increased with increasing the applied SPA. However, this has the general downside of increasing the laser processing time.

The effect of SPA was examined for IR femtosecond pulses. The SPA was varied by adjusting the galvanometer marking speed, at a fixed laser repetition rate of 5 kHz. Figure 4.15 shows the ITO on glass crater morphology at SPA’s of 2, 3, 10 and 20, at an applied fluence of 0.5 J/cm².
Figure 4.15 Surface topography for overlapped ITO on glass craters, at an applied fluence of 0.5 J/cm², with SPA’s of 2, 3, 10 and 20. Only minor improvements to the crater scribes are observed with increasing SPA

The effect of SPA can be noted in terms of the smoothness of the film removal, and the crater edge height, as observed in Figure 4.16, where the crater cross section is shown as a function of SPA.
In general, clean removal of the film is seen from 3 SPA, with only minor visible improvements to the irradiated line at 20 SPA, in the form of a decreased edge height, and minor improvements to the crater floor consistency along the line. The surface roughness along the lines has a peak to trough maximum value of 4 nm, at all applied fluences.

4.4. **ITO on glass laser pulse incubation**

Laser pulse incubation was defined in the literature review as the effect of applying multiples pulses, and is typically characterised by the incubation parameter $S$. This parameter is found by measuring the film threshold fluence for increasing number of laser shots $N$. The incubation parameter gives an indication of how the threshold fluence changes with increasing number of laser pulses. The threshold fluence decreases with increasing number of pulses if $S < 1$.

4.4.1. **Multiple pulse surface topography**

The surface topography of multi-pulse irradiation was examined, for both nanosecond and femtosecond pulses. Previously, the threshold fluence was examined as a function of pulse number, with incubation parameters of $S < 1$ found. Figure 4.17 shows the surface topography of ITO on glass craters, after 355 nm nanosecond laser irradiation, with pulse
numbers of 1, 5, and 10. The applied fluence of each pulse is 1.55 J/cm². At shot number N=1, minor glass damage of 10 nm is noted.

![Image](image_url)

Figure 4.17 (a) ITO on glass with after 10 shots, with an applied fluence of 1.5 J/cm². (b) Crater topography for shot numbers of 1, 5, and 10. Subsequent pulses leave successive re-solidified melt ridges, with no increase in ablation depth

The surface topography of the laser craters shows a high dependence on the number of laser pulses incident on the film. A circular defined re-solidified crater ridge can be seen after one pulse, in this case a depth of with 10 nm of glass to the substrate. The surface topography after 5 laser pulses undergoes changes in terms of the re-solidified ridges. Secondary ridges are not observed at the previous pulse ridge, with successive ridges forming concentric circles. No further glass damage to the substrate is observed, with a total depth of 30 nm. This is again further seen after 10 laser pulses, with further re-solidified ridges observed. Again, the glass damage to the substrate does not increase.
Increasing number of pulses causes the crater diameter to increase, resulting in re-solidified melt ridges, the amount of which is dependent on the number of laser pulses incident on the material.

The effect on the surface topography was also examined for 1030 nm femtosecond pulses, as seen in Figure 4.18. The laser pulse numbers are for 1, 3 and 10, at an applied fluence of 0.94 J/cm².

![Figure 4.18 Surface topography for shots number of 1, 3 and 10, for ITO on glass, using IR fs pulses at an applied fluence of 0.94 J/cm². Damage to the glass substrate increases with increasing pulse number](image)

As the laser pulse number is increased, a number of changes to the surface topography is noted. The damage to the glass substrate increases with the number of shots. At a pulse number of 1, selective removal of the film is noted. Glass damage of 10 and 60 nm are can be seen, for pulse numbers of 3 and 10. The ridge is not discernible at pulse numbers of 3 and 10.

### 4.5. Determination of the threshold fluence properties of ITO on glass

The threshold fluence for ITO on glass was measured using the experimental method described in section 3.2.2. The crater diameters were measured across a range of applied
laser pulse energies for each of the laser sources. The spot radius was first determined in each case, from the slope of the of $D^2$ versus the natural log the pulse energy $lnE_p$. From this, the fluence value for each pulse duration could be determined. The threshold fluence was then found from equation (34), by plotting $D^2$ versus the $ln\phi_0$, and extrapolating the linear fit to zero. The effect of a number of factors on the threshold fluence was examined, including pulse duration, wavelength, pulse number, spot radius and numerical aperture.

4.5.1. Threshold fluence of ITO on glass for nanosecond pulses

Figure 4.19 shows plots of $D^2$ versus the natural log of the fluence for pulse durations in the ns time regimes. Experimental uncertainties were taken into account using the average value of the measured crater diameter and an estimated error on the pulse energy. In general, calculated errors on the calculated spot radius were typically less than 5%. This gave accuracies on the focussed ablation threshold calculation in the range of 5-9% for each of the different numerical apertures investigated in this study.

![Figure 4.19 Fluence dependence of the crater diameter squared with for ns pulse durations, at wavelengths of 266, 355, 532 and 1064 nm](image)

Table 13 presents the calculated values for the threshold fluence, spot radius and numerical aperture, across the range of wavelengths used, with nanosecond pulse durations, taken from the data in Figure 4.19.
Table 13 Relationship between the threshold fluence, spot radius and numerical aperture for ns pulse durations at various applied wavelengths

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Threshold Fluence (J/cm²)</th>
<th>Spot Radius $\omega_0$ (μm)</th>
<th>Numerical Aperture (NA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>266 (8.6 ns)</td>
<td>0.83 ± 0.09</td>
<td>5.70 ± 0.34</td>
<td>0.033</td>
</tr>
<tr>
<td>355 (20 ns)</td>
<td>1.2 ± 0.09</td>
<td>6.49 ± 0.21</td>
<td>0.031</td>
</tr>
<tr>
<td>532 (9 ns)</td>
<td>4.85 ± 0.85</td>
<td>20.8 ± 0.2</td>
<td>0.027</td>
</tr>
<tr>
<td>1064 (9.2 ns)</td>
<td>2.38 ± 0.13</td>
<td>20.1 ± 0.8</td>
<td>0.019</td>
</tr>
</tbody>
</table>

The threshold fluence of the ITO film is shown to vary with the applied wavelength in the nanosecond time regime. The lowest observed applied threshold fluence is at 266 nm, followed by 355 nm, then 1064 nm. The highest threshold fluence is seen at 532 nm.

4.5.2. Estimation of the absorbed threshold fluence

As the film thickness used in this case is much smaller than the absorption depth ($d_{film} = 20 \text{ nm} \ll 1/\alpha_{355 \text{ nm}} = 230 \text{ nm}$), only a fraction of the applied laser fluence is absorbed in the film. The absorbed threshold fluence $\phi_{ath}$ is a parameter which can used to determine the actual energy used to ablate the film, taking into account the film reflectivity $R$, and the fraction of energy absorbed through the absorption coefficient. The formula for this is given by $\phi_{ath} = \phi_{th}(1 - R)(d_{film}\alpha)$. $(1 - R)$ is the portion of the energy not reflected at the air/film interface, and $(d_{film}\alpha)$ is the fraction of energy absorbed in the film. In this case, the absorption coefficients and reflectivity were taken from the reflectivity and transmission values obtained calculated in Table 12. The energy of the applied photon in Joules (J) is dependent on the applied laser wavelength, and is determined from the formula $E = hc/\lambda$, where $h$ is Planck’s Constant, and $c$ is the speed of light. This gives photon energies of $7.47 \times 10^{19}, 5.60 \times 10^{19}, 3.74 \times 10^{19}$, and $1.87 \times 10^{19}$ J for wavelengths of 266, 355, 532 and 1064 nm. This can be converted to eV by dividing by $1.602 \times 10^{19}$ J, giving energies of 4.66, 3.50, 2.33 and 1.17 eV, for wavelengths of 266, 355, 532, and 1064 nm. The absorbed threshold fluence is plotted against the laser photon energy in Figure 4.20.
Table 14 shows the calculated absorbed threshold fluence as a function of the applied photon energy.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Threshold Fluence (J/cm²)</th>
<th>Absorption Coefficient ($m^{-1}$)</th>
<th>Reflectivity</th>
<th>Absorbed Threshold Fluence (mJ/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>266 (8.6 ns)</td>
<td>0.83 ± 0.09</td>
<td>$2.3 \times 10^7$</td>
<td>0.32</td>
<td>443 ± 18</td>
</tr>
<tr>
<td>355 (20 ns)</td>
<td>1.2 ± 0.09</td>
<td>$4 \times 10^6$</td>
<td>0.28</td>
<td>70.5 ± 3.4</td>
</tr>
<tr>
<td>532 (9 ns)</td>
<td>7.42 ± 0.85</td>
<td>$9 \times 10^5$</td>
<td>0.1</td>
<td>68.7 ± 5.2</td>
</tr>
<tr>
<td>1064 (9.2 ns)</td>
<td>2.38 ± 0.13</td>
<td>$1.2 \times 10^6$</td>
<td>0.01</td>
<td>50.2 ± 2.6</td>
</tr>
</tbody>
</table>

Taking into account the reflected and absorbed component in the film, the absorbed threshold fluence shows the largest value at 266 nm, with the other wavelengths, which are below the ITO bandgap, showing a large decrease compared to the 266 nm pulse. The fraction of the energy absorbed in the film shows a roughly 10 fold decrease when going from 266 nm to wavelengths below the bandgap.
4.5.3. Ultrashort ITO on glass threshold fluence

The threshold fluence for ITO thin film was measured at femtosecond and picosecond pulse durations, at wavelengths of 343, 515 and 1030 nm. Figure 4.21 shows the variation in the crater diameter with the applied fluence, for the ultrashort pulse durations used.

![Figure 4.21](image)

Table 15 shows the calculated values for the threshold fluence and absorbed threshold fluence for ultrashort laser pulses.

Table 15 Relationship between the applied wavelength, threshold fluence, and absorbed threshold fluence

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Photon Energy (eV)</th>
<th>Threshold Fluence (J/cm²)</th>
<th>Absorption Coefficient (m⁻¹)</th>
<th>Absorbed Threshold Fluence (mJ/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>343 (fs)</td>
<td>3.6</td>
<td>0.25 ± 0.02</td>
<td>3.2 × 10⁶ m⁻¹</td>
<td>12.5</td>
</tr>
<tr>
<td>515 (fs)</td>
<td>2.4</td>
<td>0.57 ± 0.04</td>
<td>9 × 10⁵ m⁻¹</td>
<td>9.68</td>
</tr>
<tr>
<td>1030 (fs)</td>
<td>1.2</td>
<td>0.32 ± 0.03</td>
<td>1.2 × 10⁶ m⁻¹</td>
<td>7.50</td>
</tr>
<tr>
<td>343 (ps)</td>
<td>3.6</td>
<td>0.35 ± 0.02</td>
<td>3.2 × 10⁶ m⁻¹</td>
<td>17.5</td>
</tr>
<tr>
<td>515 (ps)</td>
<td>2.4</td>
<td>0.89 ± 0.06</td>
<td>9 × 10⁵ m⁻¹</td>
<td>15.12</td>
</tr>
<tr>
<td>1030 (ps)</td>
<td>1.2</td>
<td>0.39 ± 0.02</td>
<td>1.2 × 10⁶ m⁻¹</td>
<td>10.1</td>
</tr>
</tbody>
</table>
The threshold fluence shows a dependence on the applied wavelength for fs and ps pulses. The lowest observed threshold fluence was at 343 nm, followed by 515 and then 1030 nm, for both fs and ps pulses. The threshold slightly increases when the pulse duration is increased. Taking into the account the absorption coefficient and film reflectivity, the absorbed threshold fluence shows the opposite result, with the lowest absorbed threshold fluence now at 1030 nm. A general increase is observed in the absorbed threshold fluence as the photon energy is increased in the ultrashort pulse duration region.

4.5.4. Dependence of the threshold fluence on numerical aperture

The effect of the numerical aperture of the system was investigated for nanosecond pulses, using the 355 nm laser setup described in section 3.1.2. The numerical aperture defines the propagation angle of the laser pulse to the surface, and therefore the laser spot radius \( \omega_0 \). The numerical aperture is given by the formula \( NA = D/2f \), where \( f \) is the focal length and \( D \) is the beam diameter before the lens. The NA was varied by changing the beam diameter before the lens, using a variable aperture. In this case three NA’s were tested, 0.031, 0.015 and 0.009, giving spot radii of 6.90, 13.43 and 22.74 \( \mu \)m. The threshold fluence for the 20 nm ITO film was calculated by plotting the crater diameter squared versus the natural log of the fluence, as seen in Figure 4.22.

![Figure 4.22](image)

Figure 4.22 Dependence of the laser threshold fluence on the applied NA, for ITO thin films on glass

The values of the calculated threshold fluence can seen in Table 16, along with the numerical aperture used in each case.
Table 16 Relationship between the numerical aperture, spot radius and threshold fluence for 20 nm ITO on glass using 355 nm nanosecond pulses

<table>
<thead>
<tr>
<th>Numerical Aperture (NA)</th>
<th>Spot Radius ( \omega_0 ) (( \mu m ))</th>
<th>Threshold Fluence (J/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.031</td>
<td>6.9 ± 0.34</td>
<td>1.2 ± 0.09</td>
</tr>
<tr>
<td>0.015</td>
<td>13.43 ± 0.51</td>
<td>0.79 ± 0.05</td>
</tr>
<tr>
<td>0.009</td>
<td>22.72 ± 1.2</td>
<td>0.68 ± 0.04</td>
</tr>
</tbody>
</table>

As the NA is decreased and the spot radius is increased, the calculated threshold fluence decreases. Larger spot radii result in lower threshold fluences for the 20 nm ITO film, for the three NA’s tested. In order to fully study the relationship between the applied spot radius and film threshold fluence, a tilted plane system was used to vary the spot radius over a large range.

4.5.5. Threshold fluence dependence on the applied spot radius for nanosecond pulses

Figure 4.23 shows the nanosecond experimental threshold fluence \( \phi_{th} \) calculated using equation (36), versus the spot radius \( \omega(z) \), calculated using (3). The applied wavelength in this study was at 355 nm, using the tilted plane configuration described in section 3.2.3. Three NA’s were tested with values of 0.021, 0.032, and 0.039.
As the spot radius for the 355 nm pulses is increased, the threshold fluence shows an initial increase up to a spot radius of 7 µm. When the spot radius moves beyond this value, the threshold fluence starts to decrease almost linearly with increasing spot radius. Comparing the initial and final spot radii and threshold fluences, as the spot radius increases from 6.4 to 21.6 µm, a 3.38 fold increase, the threshold fluence decreases from 1.52 to 0.42 J/cm², a 3.61 fold decrease. Varying the NA changes the threshold fluence through shifting the threshold fluence curve. Larger NA’s, cause the change in threshold fluence to shift to the left, to lower thresholds. Lower NA’s cause a shift to the right, to higher thresholds. Comparing the threshold fluence at an equivalent $\omega(z)$ spot radii of 13 µm, for NA’s of 0.039, 0.032, 0.021, gives experimental threshold fluences of 0.7, 0.9 and 1.06 J/cm² respectively.

4.5.6. Threshold fluence dependence on the applied laser spot radius for ultrashort pulses

Using the same tilted plane method to determine the threshold fluence for the ns pulses shown in section 4.5.5, the threshold fluence was also determined at varying $\omega(z)$ for picosecond and femtosecond pulses, at a wavelength of 1030 nm. Figure 4.24 shows the
threshold fluence as function of $\omega(z)$ for both picosecond and femtosecond pulses, at the 1030 nm wavelength.

![Graph showing threshold fluence as a function of spot radius for ps and fs 1030 nm laser pulses. A linear increase in the threshold fluence with applied spot radius is seen.]

The experimental threshold fluence increases, as the spot radius is increased in the tested range and is fitted in this case with a trend $\phi_{th} = A \omega z^2$. The threshold fluence for ps pulses increases from 0.26 to 0.62 J/cm², as the spot radius is increased from 16.8 to 30.4 μm. The threshold fluence for femtosecond pulses increases from 0.23 to 0.48 J/cm², as the spot size is increased from 17.1 to 30.3 μm.

4.5.7. Laser pulse incubation using nanosecond and femtosecond pulses

The effect of multiple pulses on the ITO film threshold fluence was examined, using 355 nm nanosecond pulses. Multiple pulses at numbers of 1, 3, 5, and 10 pulses were examined. The threshold fluence for each pulse was measured by plotting $D^2$ versus the natural log of the fluence and extrapolating the linear fit to zero. Figure 4.25 shows $D^2$ versus the natural log of the fluence for pulse numbers of 1, 3, 5 and 10.
Figure 4.25 Crater diameter squared versus the natural log of the fluence for pulse numbers of 1, 3, 5 and 10. A linear dependence is seen in all cases.

The calculated threshold fluence shows a decrease with increasing number of laser shots. The incubation parameter can be calculated by plotting the natural log of the product of threshold fluence and the number of shots, versus the natural log of the number of shots, as shown in equation (32). This procedure was repeated for three different spot radii, consisting of 6.9, 13.4 and 22.1 μm respectively. Figure 4.26 shows the calculation of the incubation parameter for various spot radii.

Figure 4.26 Calculation of the incubation parameter for laser spot radii of 6.9, 13.4 and 22.1 μm. The incubation parameter increases with decreasing spot radii.
The calculated incubation parameter is < 1, which indicates that increasing number of pulses results in a lower material threshold fluence, for all the applied laser spot radii. Incubation parameters of 0.94 ± 0.09, 0.84 ± 0.02 and 0.72 ± 0.04 were calculated for spot radii of 6.9, 13.4 and 22.1 µm respectively. Firstly, an incubation parameter of < 1 indicates a lowering of the threshold fluence with increasing number of pulses. This lowering of the threshold fluence has to be attributed to either a decreasing of the material reflectivity, or an increasing of the material absorption coefficient with increasing pulse number. The applied spot radius, which determines the nanosecond laser fluence, as discussed in section 4.5.5, also is an important factor in determining the incubation parameter. Increasing the laser spot radius, resulting in a decrease in the material incubation parameter,

The incubation of the laser pulses was investigated for IR femtosecond laser pulses. The threshold fluence was calculated for pulse numbers of 1, 2, 3, 5, 10 and 20. Figure 4.27 shows the calculation of the incubation parameter S for IR femtosecond pulses.

![Graph showing incubation parameter](image)

Figure 4.27 Dependence of the threshold fluence on the number of shots, using IR fs pulses

The slope of the graph was calculated to be 0.79 ± 0.1. Therefore, as the pulse number is increased, the threshold fluence for each subsequent pulse decreases.
4.6. Substrate glass damage

The damage of the glass substrate is recognized as non-selective ablation of the ITO film, accompanied by the removal or damage to the substrate which is visible under microscopy.

Figure 4.28 2D grayscale surface profile of the ablated crater produced by UV ns laser in low overlap conditions (left). Cross sectional line profiles of sections, represented in image on left (right).

As the fluence is increased beyond the threshold fluence, the glass substrate can be damaged. The increase in glass damage was examined in terms of the applied fluence, wavelength and pulse duration.

4.6.1. Substrate glass damage using nanosecond laser pulses

As shown in Figure 4.19, the threshold fluence for ITO on glass has a strong dependence on the applied wavelength, with large variations in the threshold fluence across the range of wavelengths used. Therefore, in order to compare the effect of wavelength on glass damage, the fluence values must be normalized, taking into account the material threshold fluence and plotted against the ablation depth $d$. This allows a more valid comparison between the laser wavelengths, which show large differences in the threshold fluence.

$$d = \alpha \ln \left( \frac{\phi_0}{\phi_{th}} \right)$$  \hspace{1cm} (39)
Figure 4.29 shows the relationship between the single pulse ablation depth and the normalised fluence calculated using equation (39), for nanosecond laser wavelengths of 266, 355, 532 and 1064 nm. In general for all applied wavelengths, glass damage increases with applied fluence. The relative position of the normalised increase in damage shifts, depending on the applied wavelength. 532 nm laser pulses are shifted farthest to the left, indicating the fastest increase in glass damage with normalised fluence. Shifting to the right from 532 nm, 355 nm has the next fastest increase, with 1064 and 266 nm coming next. This indicates that glass damage has factors which are wavelength and fluence dependent.

The typical surface profile of the glass damaged ITO crater is shown in Figure 4.30, at an applied fluence of 1.8 J/cm² and at a wavelength of 355 nm. The total ablation depth is 60 nm, indicating 40 nm of glass damage.
The resulting crater shows extensive re-deposited matter in the crater, indicating ejection of material has taken place. Large variation in the size of the re-deposited particles is observed, as shown in Figure 4.31.
The average nanoparticle diameter was measured to be $162 \pm 10 \text{ nm}$. Typically, glass as a wide bandgap dielectric requires large fluence inputs in order to initiate ablation, typically in the region of $30 \text{ J/cm}^2$ [185]. Dielectric glass ablation is observed at very low fluences, beginning at $1.55 \text{ J/cm}^2$ for $355 \text{ nm } 20 \text{ ns}$ pulses. Placing a thin conductive layer on a dielectric causes the laser induced breakdown threshold of the dielectric to reduce dramatically, leading to ejection of debris, which results in re-deposited matter in the crater.

### 4.7. ITO on PET nanosecond pulsed laser irradiation

The laser patterning results are examined for $30 \text{ nm ITO}$ on flexible $0.3 \text{ mm PET}$ substrates, using nanosecond and femtosecond laser sources. A range of parameters are examined, including the effect of laser pulse duration, wavelength, number of pulses and laser spot overlap. The crater surface topography and laser threshold fluence are identified. The ability of the laser source to selectively remove from the substrate is a key factor in the process.
4.7.1. ITO on PET nanosecond laser crater morphology

The ITO on PET crater morphology was imaged using AFM, across all four nanosecond laser wavelengths. Figure 4.32 shows the crater morphology of ITO on PET craters at wavelengths of 266, 355, 532 and 1064 nm. The applied fluence in each case is chosen to best represent selective removal of the film from the substrate.

The surface characteristics of ITO craters across the wavelengths show a number of similar features, however differences in the craters are only observed for direct bandgap pulses at 266 nm. The edge of the crater in all applied wavelengths is rough and fragmented, especially at 266 and 1064 nm. A flat crater floor is observed at 355 and 532 indicating selective removal of the film. The observed crater floor at 1064 nm is very rough, with a textured appearance. No melt ridge or re-deposited nano-particles were observed in the ablated region. Figure 4.33 shows the surface topography cross section for the non-direct bandgap transition wavelengths, at 355, 532 and 1064 nm.
Selective removal of the film from the substrate is clearly observed at 355 and 532 nm, with minimal crater edges. The crater edge at 1064 nm has a large dependence on the position around the crater edge. Certain areas show smooth removal, as shown in Figure 4.33, however at other areas high fragmented edges result in total heights in the region of 100 nm. The crater floor observed at 1064 nm shows large variation across the crater, with a highest peak to trough roughness of 20 nm. This is due to the textured appearance of the crater floor, as shown in Figure 4.34, shown alongside the crater floor after 355 laser irradiation, and the crater edge after 532 nm laser irradiation.
Figure 4.34 (a) ITO on PET textured crater floor after 1064 nm irradiation at an applied fluence of 1 J/cm² (b) ITO on PET crater floor after 355 nm laser irradiation at an applied fluence of 0.8 J/cm² (c) ITO on PET crater edge after 532 nm nanosecond laser irradiation with an applied fluence of 4 J/cm²

The resulting crater floor for 1064 nm nanosecond pulses is textured in appearance, with a peak to value maximum of 20 nm. In contrast, at 355 nm, the crater floor is much smoother in appearance.
At 266 nm, a direct band to band ITO absorption process, a number of different surface features were observed, which had a large dependence on the applied laser fluence. Figure 4.35 shows the ITO on PET crater morphology at a wavelength of 266 nm, at three applied fluences of 0.8, 1.7 and 2.2 J/cm².

Figure 4.35 ITO on PET craters at applied fluences of (a) 0.8 J/cm², (b) 1.7 J/cm², (c) 2.2 J/cm² and (d) showing the side profile for an applied fluence of 1.7 J/cm², with 150 nm damage to the substrate. Non-selective removal of the film from the substrate is observed, along with ripples structures from 1.7 J/cm².

Overall, the crater morphology shows major changes compared to the other applied wavelengths. Non-selective removal of the film is seen at all applied fluences. Ripple structures can be seen on the exposed PET substrate, at an applied fluence of 1.7 J/cm² and 2.2 J/cm². The crater edge is rough and jagged, with no evidence of a melt zone or melt flow. The ripple structure was investigated in terms of the ripple depth and period, at an applied of fluence of 4 J/cm², as seen in Figure 4.36.
Examining the ripple structure in Figure 4.36, the period of the ripples was determined to be 563 ± 28 nm. The ripple depth varied from 70 – 120 nm. In general for periodic structures, the period of the ripples for an s-polarized laser is given by (31). Using this equation to calculate the ripple period, should result in a ripple periodicity of ≈ 200 nm. In this case, the ripple period is 2.8 times the theoretical ripple periodicity. Typically for ripple formation on polymer materials, the applied fluence is generally very low, typically below 10 mJ/cm² and with a large number of incident laser pulses, generally in the region of 5000 – 10000 pulses [148, 186]. In this case, ripples were obtained in the fluence region of 1.7 to 4 J/cm², much larger than other reported cases. Ripple periodicities in the region of 2λ have been obtained in the literature by using laser incidence angles of 45° [187].

4.7.2. Ultrashort ITO on PET film removal

The removal of ITO on PET thin films was examined in the ultrashort time regime, using femtosecond pulses, at laser wavelengths of 343 and 1030 nm. The surface topography was examined in terms of selective removal of the film, and the overall quality of the film
removal. Figure 4.37 shows the surface topography of ITO on PET craters using UV femtosecond pulses, for three applied fluences, at 0.4, 0.8 and 1.2 J/cm².

![Figure 4.37 UV femtosecond ITO on PET ablation craters at (a) 0.4 J/cm², (b) 0.8 J/cm² and (c) 1.2 J/cm². Non selective removal of the film from the substrate is observed at all applied fluences](image)

In all cases, non-selective removal of the film is seen. The surface topography shows a dependence on the applied fluence. Just above the threshold fluence, at 0.4 J/cm², the film edge is quite rough, with circular structures visible in the crater itself. Increasing the applied fluence to 0.8 J/cm², results in a more defined ablation crater. The exposed PET substrate is rough in texture. The crater edge is large, with a rough texture also. The exposed PET substrate has visible extrusions running perpendicular to the crater. These extrusions are not due to laser substrate interaction, but are developed during fabrication of the PET substrate. As the applied fluence is increased further, to 1.2 J/cm², the surface topography changes again. Spherical ring structures are visible in the exposed PET crater. The periodicity of the structures is approximately 1 µm.

The surface topography of ITO on PET films was also examined using IR femtosecond pulses. Figure 4.38 shows the surface topography at an applied fluences of 0.8 J/cm².
At low applied fluences, as seen here for 0.8 J/cm², selective removal of the film from the substrate is seen. Minor modifications to PET substrate can be seen, with a very light circular structure visible on the exposed PET. This is due to expansion of the PET with a height of 5 nm. The crater edge is very cleanly removed, with no cracking or fragmentation occurring. No heat effect zone can be seen around the crater edge.

4.7.3. ITO on PET threshold fluence in the nanosecond and ultrashort time regime

The threshold fluence for the ITO film on PET was calculated at wavelengths of 266, 355 and 532 nm, using the HIPPO nanosecond laser described in section 3.1.3. The threshold fluence was calculated by plotting $D^2$ versus the natural log of the fluence. This process was repeated across all four wavelengths. Figure 4.39 shows a plot of $D^2$ versus the natural log of the fluence for wavelengths of 266, 355 and 532 nm and 1064 nm. The values for ITO on glass at 355 nm are also included for comparison.
Figure 4.39 Dependence of the crater diameter squared on the natural log of the fluence for 355, 266 and 532 nm nanosecond pulses incident on ITO thin films on PET.

In general, a linear relationship is seen between the crater diameter and the applied fluence. The calculated threshold for all the applied wavelengths is shown in Table 17.

Table 17 Calculated spot radii and threshold fluences for ITO on PET, at wavelengths 266, 355, 532 and 1064 nm.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Spot Radius $\omega_0$ (μm)</th>
<th>Threshold Fluence (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>266</td>
<td>6.20 ± 0.63</td>
<td>0.18 ± 0.05</td>
</tr>
<tr>
<td>355</td>
<td>8.63 ± 0.41</td>
<td>0.32 ± 0.02</td>
</tr>
<tr>
<td>355 (ITO on glass)</td>
<td>6.9 ± 0.4</td>
<td>1.37 ± 0.09</td>
</tr>
<tr>
<td>532</td>
<td>13.1 ± 1.16</td>
<td>3.50 ± 0.49</td>
</tr>
<tr>
<td>1064</td>
<td>15.46 ± 1.03</td>
<td>0.62 ± 0.08</td>
</tr>
<tr>
<td>343 (fs)</td>
<td>15.2 ± 0.4</td>
<td>0.25 ± 0.02</td>
</tr>
<tr>
<td>1030 (fs)</td>
<td>19.36 ± 0.43</td>
<td>0.26 ± 0.03</td>
</tr>
</tbody>
</table>

At the UV wavelengths of 266 and 355, the threshold fluence shows calculated values of 0.18 and 0.32 J/cm². Increasing the wavelength to 532, results in a large increase in the
threshold fluence, up to 5.62 J/cm². The threshold fluence at 1064 nm decreases to 0.62 J/cm², in general following the same trend as the ITO on glass threshold fluences, shown in Figure 4.19, and Figure 4.21.

4.7.4. ITO on PET nanosecond incubation

The incubation of laser pulses was previously determined for ITO on glass, using 355 nm ns pulses, as seen in section 4.5.7. Incubation of 355 nm nanosecond laser pulses was also investigated for ITO on PET substrates, using the same method. The threshold fluence was calculated for laser pulses of number 1, 2, 3, 5, 10 and 20. The natural log of the threshold fluence multiplied by the number of pulses, was then plotted against the natural log of the number of pulses. Figure 4.40 shows the calculation of the incubation parameter for ITO on PET, using 355 nm nanosecond pulses.

A linear trend was fitted to the data, and the slope determined the incubation parameter, giving a value of $S = 1.18 \pm 0.05$. As the incubation parameter was found to be $> 1$, the threshold fluence increases with increasing number of pulses. This is in contrast to ITO on glass, which had an incubation parameter ranging from 0.94 – 0.72, as shown in Figure 4.25. The surface morphology of the craters for increasing pulse number is shown in Figure 4.41. Overall, no observable change in the surface morphology is seen for increasing pulse number. No increase in film or substrate damage is noted.
As the film is completely removed by the first laser pulse, the incubation properties of the PET substrate must determine how the pulses incubate. As the ITO film is a highly absorbing part of the film-substrate system, after removal of the film, the absorption properties of the system will change. An increasing threshold fluence, may be due to the lack of an absorbing film for the subsequent laser pulses. Other effects which may play a role, such as increasing reflectivity of PET substrate due to increased roughness after laser irradiation, or lowering of laser absorption in the substrate for subsequent pulses. Either way, the current widely used incubation model could be argued to be not suitable for describing thin film and substrate systems, which are both highly absorbing, as is the case for ITO and PET.

4.7.5. ITO on PET overlapped pulses

The effect of SPA on the laser crater morphology of ITO on PET was investigated using 355 nm ns pulses. The SPA was varied by adjusting the galvanometer mark speed at a fixed repetition rate of 20 kHz. The crater topography of the ITO on PET line is shown in Figure 4.41. No increase in substrate damage is observed with increasing number of pulses.
in Figure 4.42, for 355 nm nanosecond laser pulses, along with 1030 nm femtosecond pulses.

![Figure 4.42 ITO on PET overlapped pulses, at a wavelength of 355 nm and applied fluence of 0.8 J/cm², at overlaps of (a) 2 SPA (355 nm ns), (c) 5 SPA (355 nm ns) and (d) 3 SPA (1030 nm fs)](image)

Selective removal of the film from the substrate is seen in all cases. The shots per area has no effect overall on the substrate damage or edge quality for nanosecond applied pulses. Using ultrashort pulses results in a slight smoother edge, however general visible structure of the craters is the same. Selective removal of the ITO film for line formation can be achieved at SPA’s of 3. This is contrast to the results for ITO on glass, where due to the thermal process, high SPA’s of up to 10 were required for smooth selective removal of the film, as seen in Figure 4.15.

### 4.8. ITO plasma generation

The generation of a laser plasma consisting of ions and electrons was monitored in real time using the plasma generation visualisation setup described in section 3.4, using both incident nanosecond and femtosecond laser pulses. The objective of this experiment was to observe in real time the removal of any plasma or particles for the surface of the film, in order to further inform the ablation mechanism of the ITO film. The plasma evolution at a range of laser fluences was measured, from the selective removal of the film at the laser threshold fluence, to damage to the glass substrate at higher fluences. The plasma was monitored at 5-10 ns intervals after laser irradiation, until the plasma was no longer visible. By using extended CCD delays into the µs time regime, and extended camera
exposures, the nanoparticle particle emission can also be imaged. The effect of substrate on the plasma emission was also examined, with glass and PET substrates tested.

4.8.1. Laser ejected plasma for ITO on glass using nanosecond laser pulses

In the case of ITO on glass, detectable plasma was only observed at fluences well above the threshold fluence. No detectable plasma was observed for selective removal of the film from the substrate. Plasma emission was only observed at applied fluences which lead to damage to the glass substrate. Figure 4.43 shows the plasma evolution up to a time of 80 ns, for a nanosecond laser pulse with an applied fluence of 5 J/cm² at a wavelength of 355 nm.

The plasma lifetime is dependent on the applied fluence, in this case, at 5 J/cm², the plasma has a lifetime of 80 ns. The highest intensity of the plasma occurs at times between 5 and 20 ns. During this time, the nanosecond laser pulse is still on, and there likely to be an interaction between the pulse and plasma, known as laser plasma shielding. The plasma emission then begins to accelerate away from the surface at times of \( t_0 + 20 \) ns, and forms a mushroom cloud at \( t_0 + 30 \) ns, when rapid de-acceleration takes place. The average
velocity of the front associated with plasma emission is 2500 m/s. The intensity of the plasma rapidly diminishes from $t_0 + 50$ ns onwards, as the ejected plasma loose energy and begin to form a more uniform intensity over the whole plasma height. At 80 ns, self emission from the plasma is no longer observable by the optics and camera used. The change in plasma height with time was examined using equation (22), with a best fit of $\tau^{0.06}$.

The incubation of laser pulses can also be examined, by investigating the emission of laser-induced plasma. This was done using the plasma imaging setup described in section 3.4.1. The plasma was generated using an applied fluence of 5 J/cm², at a wavelength of 355 nm. Figure 4.44 shows the plasma generated for pulse numbers of 1 and 2, at a time of 0 ns, the initial interaction of the pulse and ITO thin film.

![Plasma emission at 0 ns, for pulse numbers of 1 and 2, with an applied fluence of 5 J/cm². For the second pulse, the film is completely removed due the interaction between the first pulse and the ITO film](image)

**Figure 4.44**

4.8.2. Ultrashort laser plasma imaging

The ejected plasma during laser irradiation was also examined for femtosecond laser pulses. 500 fs 1030 nm pulses were focussed to ITO material surface, and the plasma was imaged using the CCD camera. The plasma was imaged at set 20 ns intervals, at various applied fluences. Information such as the plasma height and plasma velocity can be extracted from the images. Figure 4.45 shows the plasma at an applied fluence of 8.48 J/cm², at a time of 0-120 ns after laser irradiation.
Figure 4.45 ITO on glass plasma ejection, at an applied fluence of 8.48 J/cm², using IR femtosecond pulses. The main plasma component rapidly accelerates away from the surface of the film to a height of almost 0.9 mm, with a lifetime of 120 ns. Low intensity particles are observed at 1000 ns after irradiation.
The plasma shows an initial high acceleration away from the film surface. The plasma direction is vertically orientated, with little radial spread of the plasma. The plasma reaches its peak height at 120 ns. The plasma height for three applied fluences was examined over the course of 100 nanoseconds after irradiation by the femtosecond laser pulse. The three sets of data are fit with values of $\tau^n$, in order to determine the fit of the data to point blast theory shown in Figure 4.46.

![Plasma Height vs Time Graph](image)

Figure 4.46 Plasma height as a function of time, for three IR fs pulses, with fluences of 8.5, 5.4 and 2.8 J/cm².

The initial acceleration of the plasma is fast, with the height increasing rapidly in the first 20 nanoseconds. De-acceleration begins to take place, and the plasma height stabilises after this point. The average velocity of the plasma can be taken over the first 80 nanoseconds. This was done for four applied fluences of 8.5, 5.4, 2.8 and 1.4 J/cm². The average velocity range for these applied fluences is from 4900 to 10,800 m/s. The data is fitted with a linear fit. Good agreement is seen in the fluence range tested.
The intensity of the laser plasma can be found by examining the counts of the CCD camera during the plasma evolution. This allows the intensity of the plasma to be examined and compared over time. Figure 4.48 shows the peak radial intensity across the plasma, at times of 0, 20, 40, 60 and 80 nanoseconds. The applied fluence is 5.8 J/cm².

As expected the peak intensity begins to drop immediately, with the highest CCD counts recorded at 0 nanoseconds. The CCD counts become negligible after 80 nanoseconds. The vertical evolution of the plasma intensity can also be examined. Figure 4.49 shows the vertical plasma intensity evolution as a function of time, for two pulses with applied fluences of 5.4 and 8.5 J/cm².
The peak evolution of the plasma vertically shows a fluence dependence. In the case of the larger applied fluence of 8.5 J/cm², the change in the peak intensity shows an exponential decay. The plasma intensity undergoes a rapid decay in intensity, as the material is ejected away from the surface.

4.8.3. ITO on PET nanosecond plasma emission

The plasma emission from an ITO on PET sample using 355 nm nanosecond pulses is shown in Figure 4.50. The applied fluence is the same as for the ITO on glass sample, at 5 J/cm².

Figure 4.49 CCD counts of the vertical plasma evolution with respect to time, for times after the pulse of 0, 20, 40, 60, and 80 ns. The peak decay has an approximate exponential decay.
Within the first 20 ns, no detectable acceleration of the plasma takes place. However, the surface at which the plasma is at zero, the material surface, appears to be undergoing an expansion, in the positive direction away from the scale zero mark. This is again evident at 30 ns, where a sloping of the surface may be evident. At 40 ns, some visible plasma is shown to have accelerated away from the surface, however its intensity is very small.

4.9. Laser Spatial Beam Shaping

Diffractive optical elements (DOE’s) often typically consist of a phase pattern etched into a material, and can be transmissive or reflective. The phase shift imparted on the incident laser pulse causes the intensity profile to change to a designed arbitrary intensity profile, often with a high efficiency. Computer generated holography is a common numerical method for generating the phase profile [188]. Its flexibility and ease of design has advantages over refractive or amplitude elements. After the phase profile has been generated, it must be realized onto the material surface, typically by some form of etching technique. Many methods have been used to fabricate diffractive optics. Photolithography uses multiple etches and masks to define the surface pattern [189]. Other methods include diamond turning [62], laser ablation [190] and e-beam lithography [191]. These methods are typically multi-step and result in surface etch profiles in the material which are step-like. This step-like pattern reduces the overall efficiency and accuracy of the diffractive
element. This work shows a new two-step DOE fabrication method using focused ion beam (FIB) and an inductively couple plasma etch (ICPE). The optics were tested using at-focus beam profiling methods, and applied to laser removal of ITO thin films from glass substrates.

4.9.1. Phase Profile generation

The mathematical process to create the phase profiles was implemented in Matlab. The program provides a method to design a phase profile to generate any output wavefront from a given incident wave front. The basic method to design the required phase difference \( \Delta \phi(x,y) \), is given full treatment in a previous publication for 1064 nm diffractive elements [56, 192]. The final phase difference between the interference patterns calculated for both the air and silicon media represents the phase profile across the silicon surface, which causes reconstruction of the desired wavefront with a theoretical efficiency of 100\%. This is for light at an incident angle of 0°. To produce a reflective optical element for an incident angle of 45°, the phase profile must be modified to take the inclination of the diffractive element into account. The coordinate system of the inclined element becomes distorted relative to the flat element. The transformation of the flat coordinate system \( u, v \) to the inclined coordinate system \( u', v' \) is given by [193]

\[
\frac{u}{\lambda f} = f_u = \frac{u'}{\lambda r_0}, \quad \frac{v}{\lambda f} = f_v = \frac{v' \cos(\theta)}{\lambda r_0}
\]

\[
r_0 = \left[ f^2 + u'^2 + v'^2 + 2v' f \sin \theta \right]^{\frac{1}{2}}
\]

where \( f_u, f_v \) are the spatial frequencies, \( \lambda \) is the wavelength, \( f \) is the focal length and \( \theta \) is the angle of inclination of the diffractive element. Phase profiles were designed for Fresnel lens’ and tophat lens’, with a 1mm diameter, and a focal length of 20 mm. This gives a numerical aperture of \( NA = d/2f = 0.025 \). The incident light was modelled for both 0 and 45°. Figure 4.51 shows the calculated phase difference across the silicon surface for the various intended designs Fresnel lens and tophat lens designs.
4.9.2. DOE fabrication

The calculated phase profiles must be physically realised on the silicon surface as an etch height that will impart the desired phase difference. This etch height is given by

$$\Delta h = \frac{\Delta \phi(x, y) \lambda}{2\pi(2n_{air})\cos\theta}$$  \hspace{1cm} (42)

Where $\Delta \phi(x, y)$ is the phase difference calculated using CGH, $\lambda$ is the incident wavelength, and $n_{air}$ is the refractive index of air, and $\theta$ is the angle of the diffractive element. The maximum etch depth occurs when $\Delta \phi(x, y)$ is equal to $2\pi$. This gives maximum etch depth of $\Delta h = \lambda/2\cos\theta$. This gives an etch depth of 177.5 and 250.9 nm, at DOE tilt angles of 0 and 45° respectively, for an incident wavelength of 355 nm.
The fabrication of the reflective silicon DOE’s took place using a two-step fabrication method of FIB implantation (FEI Workstation 200) and followed by an ICP etch (Oxford Instruments). In order to achieve a linear blazed profile in the silicon, the relationship between the FIB implant dose \( (pC \, \mu m^{-2}) \) and plasma etch time must be determined. A 1000 pA FIB beam aperture is used, which gives a focused spot size of 112 nm. Using a fixed ICP etch of 3 min, the average differential etch for test Fresnel lens elements versus maximum implant dose can be observed. The relationship between implant dose and etch height shows a near linear dependence, therefore by varying the implant dose linearly along the desired blazed profile, a single fixed etch time produces a linear etch depth, leading to a blaze profile. For example, for an etch depth of 177.5 nm, the implant dose is varied linearly from 0 to 20 \( pC \, \mu m^{-2} \) along the blaze profile, followed by a fixed plasma etch of 3 min. Any maximum etch depth can be obtained by using the calibrated FIB implant. This allows fabrication of DOE’s for a wide variety of operating wavelengths.

![Graph](image)

Figure 4.52 Relationship between the average silicon etch depth and implanted maximum etch dose, for a fixed etch time of 3 minutes

Using the calibrated etch times, the phase profiles shown in Figure 4.51 were fabricated on the silicon surface. Figure 4.53 shows the DOE’s generated using this two-step fabrication method.
The fabricated diffractive optics show excellent blazed phase profiles and reproduction of the intended phase design. The maximum measured etch depth is 240-260 nm. This is in good agreement with the desired theoretical etch depth of 250.9 nm. Typically, etch depth errors of less than 10% show little effect on the overall efficiency of the element. A small number of “dead zone” areas can be seen on the elements, where no FIB
implantation takes place. In order to examine the surface etches in more detail, the Fresnel lens DOE was examined using atomic force microscopy. The surface roughness of the etches must be minimized in order to decrease the scattering of the incident laser pulse and maximize the DOE efficiency. The blaze profile shows a smooth etched surface, with some minor ridges of approximately 2-5 nm visible.

4.9.3. DOE laser application

In order to test the laser beam shaping properties of the DOE’s, the elements were tested using the 355 nm module of the HIPPO laser used in this study described in section 3.1.3. The 2 mm beam diameter output of the laser was reduced to 1 mm using a beam reducing telescope. A rotary 1/2 wave plate was used to control the orientation of the linear polarization incident on the DOE’s before reflecting from the diffractive optic surface. The focused beam profiles were analysed using a focused beam profiler (DataRay BeamScope – P7). Figure 4.54 shows the focused beam profiles for the Fresnel lens and tophat lens DOE’s, at the focal point of the DOE. The values are overlapped with ideal Gaussian and tophat spatial beam profiles.
The Fresnel lens focal spot as seen in Figure 4.54 (a), shows a 95 % fit to the intended Gaussian reconstruction profile, with a 1/e² spot radius of 26 µm. The tophat lens shows a FWHM diameter of 50 µm, with a 92 % fit to an ideal tophat beam. Some variation can be seen across the intended flat profile, with some minor sloping of the profile at the spot edge. This may be due to the non-ideal Gaussian input beam, which estimated to be a 90 % to an ideal Gaussian profile. This imperfection reduces the overall efficiency of the DOE that can be defined as the reflectivity of the silicon element. Theoretically, the overall reflectivity of the element can be estimated from the refractive index of silicon, which is approximately 5.2 at 355 nm. This gives a reflectivity of 54 %. As the DOE’s are orientated at 45° to the incident laser beam, the reflectivity of the element can be separated into s and p polarizations. In order to maximize the reflectivity of the element, the amount of s polarization reflection needs to be maximized. By the rotating the linear
polarization element before the DOE’s, the linear polarization can be aligned perpendicular to the plane of incidence, maximizing the reflectivity. Rotating the linear polarization by 90° results in a minimum in the reflectivity. This results in a maximum and minimum reflectivity of 53 % and 34 % respectively, measured across a range of incident laser powers. Taking the maximum reflectivity, this results in a 1st order diffraction efficiency in excess of > 95 %.

4.9.4. DOE application to ITO thin film removal

The application of the tophat DOE’s for laser processing was tested using on ITO thin films on glass. The surface profile was examined for both Fresnel lens and tophat lens at an applied wavelength of 355 nm.

Figure 4.55 ITO on glass surface craters formed after laser irradiation using Fresnel lens and tophat lens DOE’s, at the ITO on glass threshold fluence
Film removal of ITO on glass using the Fresnel lens Gaussian distribution leads to the typical crater cross section observed using the standard Gaussian lasers in this study. Re-solidified crater ridges are observed at the crater edge, along with the clean selective removal of the film from the substrate. The crater topography of the ITO crater for tophat distribution shows no re-solidified crater ridge, with a surface topography similar to craters observed at large spot radii in Figure 4.7. The tophat laser beam results in homogenous temperature distribution on the film surface, which results in no fluid flow to the crater edge. Overall, the diffractive optical elements show good potential for laser film processing due to the observed lack of a re-solidified melt ridge. This will lead to relaxation of the SPA criteria for smooth processing, as potentially very low SPA will be required to complete the resulting crater line. This would lead to an increased processing speed and material throughput.

4.10. Chapter Conclusions

The preceding chapter showed the results of laser patterning of ITO on glass, and ITO on PET using nanosecond, picosecond and femtosecond pulse durations, across a range of wavelengths and optical delivery conditions. The following conclusions from this chapter are as follows

- The laser threshold fluence for ITO on glass for pulses is dependent on a range of material and laser properties
  A number of factors such as wavelength, pulse duration, NA, spot radius and number of laser pulses define the laser material interaction. As the threshold fluence is measured in terms of the applied energy density, the absorbed component in the film can vary depending on a number of factors. The laser threshold fluence depends on the applied wavelength, due to the change in the absorption coefficient. Shorter laser pulse durations result in a decreasing threshold fluence, as the applied laser energy is confined to the very thin film. The laser spot radius for both nanosecond and ultrashort laser pulses effects the laser threshold fluence. Larger spot radii result in smaller threshold fluences for nanosecond laser pulses. The opposite condition applies for ultrashort laser pulses, where the threshold fluence increases with increasing spot radii.
The threshold fluences dependence on the wavelength is determined by the material reflectivity and absorption coefficient

The absorbed threshold fluence of the ITO film was calculated, which takes into account the material absorbed in the film, determined from the portion reflected and absorbed in the film. The results showed that the threshold fluence in general increases with applied photon energy for laser pulses below the direct transition bandgap, except at 355 nm photons, were a decrease is observed. A large increase in the absorbed threshold fluence is noted as when the applied photon energy is greater than the ITO bandgap.

ITO film removal at the threshold fluence is a non-ablative process for nanosecond laser pulses with photon energies below the bandgap

The induced crater surface topography on the ITO film after nanosecond laser irradiation shows large re-solidified melt ridges, with no evidence of a re-deposited nanoparticles. Selective removal of the film from the substrate is observed for laser pulses with wavelengths of 355, 532 and 1064 nm. As the laser photon energy is increased above the ITO bandgap (266 nm), the surface topography undergoes a major visual change. Only a minor crater ridge is observed, along with re-deposited particles. Selective removal of the film is not observed at a wavelength of 266 nm, with 5 nm of glass damage noted at the lowest tested applied fluence.

Glass damage in the substrate occurs at fluences just above the threshold fluence, for all nanosecond laser pulses

Damage to the glass substrate increases linearly with the applied fluence, leading to re-deposited material in the crater. Glass damage occurs at all nanosecond laser wavelengths, at fluences above the threshold fluence. The glass damage across the range of wavelengths can be normalised, to take into account the differences in the threshold fluences. The slope of the increase in the glass damage with applied fluence is different for all of the wavelengths. This indicates that glass damage to the substrate is wavelength dependent.
• **The ITO on PET film under laser irradiation has a much different interaction compared to ITO on glass**

ITO on PET has a lower threshold fluence by almost a factor of 4, and a different surface morphology to ITO on glass. Selective removal of the film from the substrate is observed at wavelengths of 355, 532 and 1064nm, with a rough fragmented edge. No evidence of a melt or vaporisation phase was observed. Laser pulses at 266 nm, which are above the ITO bandgap, result in non-selective removal of the film from the substrate, with LIPPS formation on the exposed PET substrate. Clean ITO line removal can be observed at SPA’s of 2. Femtosecond laser pulses at 1030 nm can be used to selectively remove the film from the substrate, with a much smoother fragmented edge, compared to nanosecond laser pulses.

• **Selective removal of the ITO film on glass can be achieved using ultrashort laser pulses**

The ablation properties of thin ITO film on glass using ultrashort laser pulses have a much different interaction compared to nanosecond laser pulses. The overall surface topography is essentially homogenous across the range of wavelengths used, and between the femtosecond and picosecond laser pulses. Selective removal of the film from the substrate can be obtained, resulting in re-deposited nanoparticles with diameters on the order of the film grain size. No evidence of a re-solidified melt zone was noted. In-complete removal of the film was also obtained at low fluences, with a totally depth of 10 nm.

• **Custom diffractive optics were fabricated for tophat spatial beamshaping**

Reflective blazed diffractive optics were fabricated on silicon using a novel two-step fabrication method, consisting of a focused ion beam implant, and a reactive ion etch. The reconstructed beam profiles were a good fit to the intended design. Laser processing of the ITO film using the tophat spatial profile, results in a minimised crater edge.
Chapter 5

5. Computational simulation of the laser-thin film interaction

In Chapter 4 the laser-thin film interaction was examined experimentally. A number of important factors were identified in the ITO thin film surface topography such as pulse duration, wavelength, substrate material and laser spot radius. The key objectives of this chapter is to simulate the laser film interaction using computational finite element methods. In these simulations, the Fourier heat equation is solved for nanosecond pulses, and the two temperature model is solved for ultrashort pulses. The stress build up in the film was also examined under the influence of thermal expansion for long nanosecond pulses, and the electron blast force for ultrafast laser pulses.

The following key objectives were targeted

- To analyse the film removal process for nanosecond pulses, by simulating the temperature rise in the ITO thin film and glass substrate, in order to identify the molten and vaporised components during laser irradiation.

- To examine the electronic temperature rise after ultrashort laser pulse irradiation, and to examine the coupling of the electronic and lattice sub-systems. This allows the peak lattice temperature of the film to be simulated, which can be used to show any melt or vaporised zones during laser irradiation.

- To identify the lattice strain and stress in the film and substrate due to thermal expansion under laser heating, for nanosecond laser irradiation of ITO on flexible PET substrates.
To estimate the ultrafast lattice de-formation in the film, using the electron temperature and the gradient of the electron temperature in the ITO film, commonly known as the electron blast force

5.1. ITO on glass thermal simulation for nanosecond pulses

In order to determine the temporal and spatial temperature profile of an incident laser pulse of radius \( \omega_0 \) in the thin film and substrate, a finite element thermal model was developed using COMSOL’s Multiphysics finite element package. A full description of the model is given in section 3.6.1, where the optical and material characteristics are described.

5.1.1. Film temperature simulation under nanosecond pulses

The rise in the peak temperature in the ITO film on glass substrates can be examined as a function of the applied laser wavelength for nanosecond laser pulses, at the experimental applied wavelengths of 266, 355, 532 and 1064 nm. The differential heat equation given in (9) is solved using the laser heat source term given in (11). In each case, the experimental conditions were used, such as the laser pulse duration and experimental threshold fluence, along with the relevant material parameters for each applied wavelength, taken from Table 9. The peak temperature in the film could then be plotted as a function of time. The peak temperature occurs at the film surface, at the center position of the Gaussian pulse, given in spatial coordinates as \( x, y (0,0) \). Figure 5.1 shows the temporal rise in the peak temperature of the ITO film for all applied nanosecond wavelengths at the respective threshold fluences of each, taken from Table 15.
Figure 5.1 Peak temperature in the ITO film versus time, for nanosecond laser pulses at wavelengths of 266, 355, 532 and 1064 nm. The spatial laser intensity is shown for the longer 355 nm pulse, and the shorter 266 nm laser pulse. The peak temperature for non-direct band to band transition wavelengths is just at the ITO melting point, while for 266 nm direct band transitions pulses, the temperature is much greater.

The peak temperatures at the threshold fluence are shown in Table 18.

Table 18 Simulated peak ITO film temperature as a function of nanosecond laser wavelength

<table>
<thead>
<tr>
<th>Laser Wavelength (nm)</th>
<th>Threshold Fluence (J/cm²)</th>
<th>Peak film temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>266</td>
<td>0.83</td>
<td>3100</td>
</tr>
<tr>
<td>355</td>
<td>1.2</td>
<td>1950</td>
</tr>
<tr>
<td>532</td>
<td>4.85</td>
<td>1950</td>
</tr>
<tr>
<td>1064</td>
<td>2.38</td>
<td>2000</td>
</tr>
</tbody>
</table>

In the case of laser wavelengths of 355, 532 and 1064 nm reaches a temperature greater the ITO melting temperature ($T_m = 1900 \, \text{K}$). The peak temperature in the film at a wavelength of 266 nm, just reaches the estimated ITO vaporisation temperature ($T_v = 3000 \, \text{K}$). The peak value for 266, 532 and 1064 nm occurs at a time of $t_0 + 19 \, \text{ns}$ after laser irradiation. The peak value of the 355 nm laser pulse occurs at a longer time of $t_0 +$
33 ns. This longer time to reach the peak temperature is due to the longer pulse duration of the 355 nm pulse. The beginning of melting of the film takes place at total time of at 15.5 ns for the 532 and 1064 nm pulses, and at 24 ns for the 355 nm pulse. The time for melting of the full film from the onset of melting with the 355 nm pulse, is 1.1 ns, giving a melt propagation velocity of 18 ms\(^{-1}\). The difference between the front and rear side temperature of the film, at the melting temperature is approximately 30 K. At 532 and 1064 nm, the time to melt the whole film is 0.2 ns, resulting in a melt front velocity of 100 m/s. After the peak temperature, the heat in the film rapidly drops as heat conduction drives the heat to the colder substrate.

The molten recoil pressure and the rate of atomic flux can be calculated during the laser heating process, using equations (12) and (13), given as the Claus-Clapeyron and Hertz-Knudsen equations respectively. In this case, the wavelength of 266 nm is of interest, due to much higher temperatures observed, which reach the estimated vaporisation temperature. Figure 5.2 shows the peak temperature and atomic flux as a function of time, for a 266 nm pulse at the experimental threshold fluence of 0.83 J/cm\(^2\).

![Figure 5.2](image.png)

**Figure 5.2** Peak temperature and atomic flux rate as a function of time, for a 266 nm pulse at an applied fluence of 0.83 J/cm\(^2\). Particle flux begins to occur when the temperature approaches the estimated vaporization point of 3000 K.

As the peak temperature approaches \(T_v\), the rate of atomic flux beings to rapidly increase. This rapid increase begins at \(t_0 + 12\) ns, with a peak atomic flux occurring at \(t_0 + 20\) ns,
which coincides with the peak temperature observed in the film. The atomic flux only has relevant values as $T$ becomes very close to $T_v$. The atomic flux for laser pulses at all other wavelengths was negligible at the experimental threshold fluence, as the peak temperatures for these wavelengths is in the region of 1900 – 2000 K, much lower than the temperature required for significant atomic flux to begin.

5.1.2. Effect of heat conduction at the film substrate interface

The spatial distribution of the induced temperature in the film and substrate can also be examined. As the absorbing film heats up, heat conduction across the film-substrate interface region will take place due to the thin nature of the film, where the heat diffusion length is much greater than the film thickness $l_t = \sqrt{D\tau_p}$. The heat diffusion length in this case is between 406 and 266 nm for laser pulse durations of 20 and 9 ns, respectively. Heat conduction to the substrate was examined across a range of times after laser irradiation, concentrating on the 355 nm wavelength. Figure 5.3 shows the heat rise in the film and substrate for a 355 nm laser pulse, at an applied fluence of 1.3 J/cm$^2$, which corresponds to selective removal of the film experimentally. The spot radius in this case is normalised to 0.5 µm, in order to better show the interface region between the film and substrate.
Figure 5.3 Peak temperature rise in the ITO thin film and glass substrate for an incident 355 nm pulse, with an applied fluence of 1.3 J/cm² with a normalised spot radius of 0.5 µm. Significant heat conduction to the glass substrate takes place.
As the film absorbs the simulated laser pulse, the lattice heats up until the film reaches the melting temperature and phase changes begin. As the film is much thinner than the laser absorption depth, the film is heated uniformly to the substrate interface. Heating of the glass substrate is through heat conduction across the film substrate interface. At the interface between the film and substrate, the glass can reach high temperatures, with peak values similar to that observed in the film. The temperature then drops off into the substrate due to heat conduction. As the time after laser irradiation increases, the heat peak temperature in the film decreases as heat is re-distributed to the substrate. The substrate has the properties of a heat sink, with minimal direct absorption in the dielectric material due the low dielectric absorption coefficient, it acts to draw heat away from the film. The effect of heat conduction for 266 nm pulses is also shown in Figure 5.4, at the experimental threshold fluence.

![Figure 5.4 Peak spatial temperature distribution in the ITO film and glass substrate for 266 nm laser irradiation at an applied fluence of 0.83 J/cm². High temperatures are observed in the interface region between the film and substrate](image)

The overall temperature distribution is similar to that obtained using 355 nm pulses, however the temperatures observed are higher, due to the higher absorption coefficient of the 266 nm pulse. High temperatures are conducted to the substrate in the interface region, with temperatures greater than 2000 K in a 25 nm region of the glass interface. The peak temperature in the film is 3100 K.
5.1.3. Simulated UV nanosecond ITO crater diameters

Using the ITO film and substrate temperature model described in 3.6.1, the induced crater diameter on the ITO film can be estimated. Examining the peak temperature for 355 nm laser pulses in Figure 5.1, the peak temperature reaches the ITO melting temperature at the threshold fluence. This can be considered the starting point for material removal. The simulated crater diameter in the finite element simulation can be defined as the radial distance from the laser pulse centre position, where the temperature drops to the ITO melting temperature (T= 1900 K), or in the case of 266 nm, where the radial distance reach the approximate vaporisation temperature (T=3000 K). The radial temperature profile calculated in the film is shown in Figure 5.5, for 355 nm pulses, at applied fluences of 1.8, 2.9 and 3.5 J/cm². The laser spot radius is 6.9 µm, which is the experimental spot radius from the data shown in Table 15.

![Figure 5.5 Peak radial temperature in the ITO film for applied fluences of 1.8, 2.9 and 3.5 J/cm². As expected, with increasing applied fluence, the overall diameter which is greater than the melting temperature increases.](image)

At the three applied fluences used, results in radial distances greater than the melting temperature of 10.1, 13.4 and 14.9 µm for applied fluences of 1.8, 2.9 and 3.5 J/cm² respectively. This process for estimating the crater diameter can be expanded to more applied fluences. This is shown in Figure 5.6, where the simulated crater diameter is compared to the experimental crater diameter, which are taken from Figure 4.19.
Overall, good agreement is seen between the simulated and experimental crater diameters, for both 266 and 355 nm pulses, with results typically within 0.5 µm. This again shows, that for moderate applied fluences, the crater diameter is essentially determined by the point of on the Gaussian laser source, which can reach the ITO melting temperature, and overcome the ITO latent heat of melting. Despite the assumptions of the finite element model, it still provides a good approximation to the ITO film removal process. Plotting the simulated crater diameter squared versus the natural log of the applied fluence gives an estimation of the simulated applied threshold fluence. For 266 and 355 nm pulses the calculated threshold fluence values are 0.73 and 1.12 J/cm$^2$, which are close to the values obtained experimentally, at 0.83 and 1.2 J/cm$^2$ respectively.

5.1.4. Simulated change in film absorption coefficient with spot radius

As observed in Figure 4.23, the experimental threshold fluence was shown to vary with the applied laser spot radius. Lower values of spot radii result in higher thin film threshold fluences. A four-fold decrease in the threshold fluence was noted in the spot radii range of 6-22 µm for 355 nm nanosecond pulses. In the COMSOL simulations, the threshold fluence can be defined as the applied fluence required for the film to reach the melting
temperature, as shown in Figure 5.1. As shown previously, using this model, good agreement between the experimental and simulated values at small spot radii can be achieved, using the absorption coefficient and reflectivity calculated experimentally, as shown in Figure 4.2. However, as the spot radius is increased, the material parameters cannot account for the change in threshold fluence with spot radii. In this section, it is shown that the change in threshold fluence with spot radii can be simulated by increasing the film absorption coefficient, as the spot radii is increased. The input data into the simulation is the experimental threshold fluence and spot radii for an NA of 0.32, taken from Figure 4.23. The absorption coefficient of the film in the model is then adjusted until the peak temperature in the film reaches the melting temperature. The absorption coefficient at this value is then recorded. Figure 5.7 shows the computationally determined absorption coefficients, plotted as $1/\alpha$, over a range of spot radii, in order for the film to reach the melting temperature.

![Figure 5.7 Change in simulated absorption depth as a function of spot radius for 355 nm nanosecond laser pulses](image)

As the spot radius is increased, the absorption coefficient of the film must be increased, shown in the graph as $1/\alpha$, in order to reach the experimentally determined threshold fluence. In other words, the simulated absorption coefficient of the film must be increased.
5.1.5. Simulated substrate glass damage during laser irradiation

During laser heating of the highly absorbing film, large amounts of heat are conducted to the substrate. Damage to the glass substrate is observed experimentally for nanosecond laser pulses, with only a narrow process window where selective removal of the film is possible. While the exact absorption mechanisms of the glass may be complicated, here a simplified perspective of glass damage is presented, using only heat conduction. Using the temperature in the substrate as a function of depth into the material, the temperatures greater than the molten and vaporisation points can be identified. Figure 5.8 shows the simulated temperature in the film and substrate, for 355 nm nanosecond laser pulses, at various applied fluences, ranging from 2.9 to 3.71 J/cm². The applied fluences were chosen as the fluences used in Figure 4.29, which shows the increase in glass damage for various applied fluences, using nanosecond pulses at a wavelength of 355 nm, where the estimated vaporisation point of the glass substrate is given as $T_{sv} = 1800\, K$

As the applied fluence is increased, the peak temperature in the film increases, from 2000 to 2900 K, as the fluence is increased from 2.05 to 3.71 J/cm². Large amounts of heat are conducted across the boundary between the film and substrate. The temperature of the glass at the interface is the same as that at the front side of the ITO. This is due to the uniform absorption throughout the film. The heat in the glass substrate then diffuses down further into the substrate. The simulated crater depth can be found as the heat depth to which the temperature reaches the glass vaporisation temperature. The glass vaporisation
point is chosen as the reference temperature, due to the glass damage topography noted for 355 nm pulses, which consists of fragmented re-deposited particle which is evidence of an ablative mechanism. Figure 5.9 shows the simulated crater depth from the thermal heat simulations across a range of applied fluences, versus the experimental crater depth, for 355 nm nanosecond pulses.

![Graph showing experimental and simulated crater depth for ITO on glass, using 355 nm nanosecond pulses, across a range of applied fluence values](image)

Figure 5.9 Experimental and simulated crater depth for ITO on glass, using 355 nm nanosecond pulses, across a range of applied fluence values

At low values of applied fluence, specifically around the threshold fluence, good agreement can be noted between the simulated ablation depth and experimental ablation depth. As the fluence is increased further, the experimental crater depth rapidly increases, while the simulated ablation depth due to heat conduction increases at a much slower rate. An ablation depth difference of 40 nm is noted at an applied fluence of 3.5 J/cm².

### 5.2. ITO film temperature simulation: Tophat intensity profile

The standard heating model used in section 3.6, used a standard Gaussian laser source to determine the temperature distribution in the film. The effect of a square intensity profile can also be used to estimate the temperature rise in the film and substrate. The intensity profile of the laser used was altered from the normal Gaussian source, to square intensity profile.
\[ Q(x, z, t) = \frac{2\phi_0 \alpha}{\sqrt{\pi/\ln 2} t_p} (1 - R) \exp \left\{ -\left( 4\ln 2 \right) \left( \frac{t_p - t}{t_p} \right) - \exp(\alpha z) \right\} * H \]

\[ H = 1, \text{ if } r < \omega_0 \] (43)

The rectangular function \( H \) is applied to the laser intensity term \( Q \) using an if command function. The temperature profile in the film and substrate can then be compared using both laser configurations. Figure 5.10 shows the temperature distribution in the film and substrate for a 355 nm nanosecond tophat spatially distributed laser pulse, with an applied fluence of 1.4 J/cm².

![Figure 5.10 Peak temperature profile in the film and substrate for ITO on glass, for tophat beam profiles. The spot radius is normalised to 0.5 µm, to better show the region of interest, at the film substrate interface](image)

The temperature distribution in the film and substrate follows the tophat intensity distribution, with a peak temperature of 2000 K. Only a minor temperature gradient in the film is seen, due to lateral heat conduction in the radial direction. The heat conduction profile in the substrate also has a more tophat distribution, however in terms of an overall depth, the drop off in temperature is the same as for a Gaussian intensity distribution.
5.3. Two temperature model for ultrashort pulse irradiation

The two temperature model, as described in section 2.5.1, outlines the absorption of the ultrafast laser source by the electronic subsystem, and the coupling of this energy to the lattice. The two differential time dependent equations given in (14) and (15) are solved using finite element methods. The effect of wavelength and applied fluence was examined for both picosecond and femtosecond laser pulses.

5.3.1. Electron and lattice temperature at the femtosecond and picosecond threshold fluence

The electron and lattice temperature were first examined for femtosecond and picosecond laser sources, at a wavelength of 1030 nm. The experimentally calculated threshold fluence and relevant absorption coefficient was used in each case. The simulations were run until there was equilibrium between the electron and lattice temperatures. Figure 5.11 shows the estimated peak electron and lattice temperature in the ITO film for femtosecond and picosecond laser pulses, at their respective threshold fluences. The lattice temperature distribution is also shown, at the electron phonon coupling time for the applied femtosecond laser pulse.
After laser irradiation, the electron temperature rapidly increases. For the fs pulses, the peak temperature of the electrons occurs at a time when the lattice is still cold. The peak

Figure 5.11 (a) Lattice temperature distribution for 1030 nm fs pulses at the experimental threshold fluence (b) Electron and lattice temperature change with time for ps and fs 1030 nm pulses at the threshold fluence

After laser irradiation, the electron temperature rapidly increases. For the fs pulses, the peak temperature of the electrons occurs at a time when the lattice is still cold. The peak
temperature of the electrons is 27,000 K, at a time of \( t_0 + 890 \) fs. The electrons heat up much slower for the applied picosecond pulses, reaching a peak temperature of 19,600 K, at a time of \( t_0 + 15 \) ps. The electrons couple energy to the lattice after the peak temperature in the electron sub-system is reached. Heating of lattice takes place via electron-phonon coupling. The time taken for the fs and ps coupling is 16 and 26 ps respectively. The peak temperature of the lattice at the threshold fluence for femtosecond and picosecond pulses is 1050 and 1200 K, at the respective threshold fluences. In both cases, the temperature is below the melting temperature of ITO \( (T_m = 1900 \) K\).

As the applied fluence is increased further, the peak temperature in the lattice increases. This is shown in Figure 5.12, for picosecond pulses, where the electron and lattice temperatures are shown at a higher applied fluence of 1.9 J/cm², along with the inset, which shows the peak lattice temperature versus applied fluence, ranging from 0.4 – 1.6 J/cm².

![Figure 5.12](image)

Figure 5.12 Electron and lattice temperature after laser irradiation with a 10 ps 1030 nm pulse, with an applied fluence of 1.9 J/cm². The peak temperature in the lattice is simulated to be 5400 K.

At this higher applied fluence, the peak temperature in the lattice reaches 5400 K, much greater than the ITO melting temperature and vaporisation temperature. As the applied fluence is increased, the peak lattice temperature increases linearly with applied fluence. Three regions can be identified from change in peak lattice temperature with applied fluence. Firstly, from 0.2 – 0.71 J/cm, the peak temperature is below the thermal melt temperature, which indicates a non-thermal ablation region. From 0.71 – 1.3 J/cm², the
peak temperature in the film is greater than the ITO melting temperature, which indicates a thermal melt region. Finally, from upwards of 1.3 J/cm², the peak temperature is greater the ITO vaporisation temperature, which indicates a thermal ablation region.

5.3.2. Crater diameter estimation using picosecond and femtosecond pulses

The lattice temperature can also be examined in terms of its radial temperature profile across the surface of the film, for both femtosecond and picosecond pulses. Using the same method used in Figure 5.6, the simulated crater diameter can be compared to the experimental crater diameter, in this case taken from the experimental data in Figure 4.21. The simulated crater diameter is taken as the radial lattice temperature where the film temperature exceeds the film melting temperature. Figure 5.13 shows simulated crater diameter and the experimental crater diameter for 1030 nm picosecond and femtosecond pulses.

![Crater diameter estimation using picosecond and femtosecond pulses](image)

Figure 5.13 Experimental and simulated crater diameters for ITO on glass using picosecond and femtosecond pulses, across a range of applied fluences. At low applied fluences, the model cannot simulate the expected crater diameter, considering the thermal melting point as the ablation criteria.

In the low fluence regime (≤ 0.7 J/cm²), the simulated crater diameter for femtosecond and picosecond pulses is zero, as the temperature of the film does not reach the ITO melting temperature. As the fluence is increased, the simulated crater diameter increases for both femtosecond and picosecond pulse durations, and above 0.6 J/cm², better
agreement is noted between the craters. However still, large differences between the simulated and experimental are seen, with the simulated crater diameters underestimating the experimental crater diameters, by a value in the region of 10 - 20 µm. This leads to the conclusion that using the thermal melting or vaporisation temperature as the point describing laser ablation, does not account for the crater diameter observed in the film.

5.3.3. Effect of laser wavelength in the femtosecond time regime

The effect of the laser wavelength on the electron and lattice temperature was examined in the femtosecond time regime. The peak electron and lattice temperature was simulated, using the optical constants described in Table 11. Figure 5.14 shows the change in electron temperature as a function of time for 343, 515 and 1030 nm femtosecond laser pulses, at their respective experimental threshold fluences, of 0.25, 0.57 and 0.32 J/cm².

![Figure 5.14 Change in electron temperature as a function of time after 500 fs laser irradiation with wavelengths of 343, 515 and 1030nm, at the respective threshold fluences. Higher electron temperatures are noted at 343 nm](image)

The peak electron temperature is 26,900, 29,000 and 33,000 K for 1030, 515 and 343 nm pulses. In all cases, the electrons and lattice have reached a steady state temperature within 20 ps after laser irradiation. The corresponding lattice temperature is shown in Figure 5.15.
Figure 5.15 Change in lattice temperature as a function of time after 500 fs laser irradiation with wavelengths of 343, 515 and 1030nm, at the respective threshold fluences. The peak temperature for all wavelengths is less than ITO melting temperature of 1900 K.

The peak lattice temperature is found to 1050, 1160 and 1350 K, for 1030, 515 and 343 nm fs pulses. In all cases, the peak temperature in the lattice is below the ITO melting temperature.

5.3.4. Ultrafast thermo-elasticity model

The interaction of the ultrafast laser pulse is first with the electronic subsystem. The electrons are heated to high peak temperatures, much greater than the lattice temperature. As shown in Figure 5.11, the peak temperature of the electronic subsystem can reach up to 29,000 K within the first 800 fs after laser irradiation. This high electron temperature can lead to an ultrafast deformation stress in the lattice, known as the electron blast force. This electron blast is proportional to the gradient of the electron temperature squared [133], and is given by equation (29). In this section, the electron blast force is approximated for 1030 nm femtosecond laser pulses, at the experimental film threshold fluence. Figure 5.16 shows the peak electron blast force in the film, in terms of the electron gradient distribution $\frac{\partial T_e}{\partial y}$ as a function of spatial distribution and time, along with the electron and lattice temperatures at the threshold fluence (0.18 J/cm²), for 1030...
nm femtosecond pulses. The electron temperature is simulated using the TTM model, with the electron and lattice temperature shown in Figure 5.11.

The electron blast force has a peak value in the centre of the thin film, at a depth of 10 nm. The change in electron blast force is rapid throughout the film, with values approximately zero at the film surface and at the interface between the film and substrate. The electron blast force rapidly increases with time, reaching a peak value of $2.4 \times$
10^{14} N/m^2, at a time of  t_0 + 590fs, occurring before the peak the electron temperature observed in the TTM model, which is at t_0 + 890fs. As the electron temperature couples to the lattice, the electron blast force rapidly decreases. At 1 ps after irradiation, the electron blast force goes to zero. The electron blast force therefore occurs during a near thermally undisturbed lattice, resulting in a non-thermal stress in the film.

5.3.5. Effect of laser pulse duration on the electron blast force

The electron blast force calculated in section 5.3.4, is highly dependent on the electron temperature and the gradient of the electron temperature in the film. The temperature of the electrons and its gradient are a strong function of the applied pulse duration. Longer laser pulses lead to lower peak electron temperatures, more quickly leading to the eventual case of electron lattice equilibrium, typically observed for nanosecond laser pulses. As simulated in this study, 1030 nm femtosecond laser pulses can induce a strong non-thermal stress in the film, which peaks before 1 ps after laser irradiation. This stress may have a strong effect on the ablation properties of the film. The ablation properties of nanosecond pulses are mainly dominated by thermal effects, where the ablation properties of the film and substrate can be estimated using parameters such as the film melting and vaporisation temperature. Therefore, it is useful to determine the effect of the electron blast force as a function of increasing laser pulse duration, in order to determine the pulse duration where the expected transition from the non-thermal to thermal pathways begins. This was simulated using the previously described TTM model, and the ultra-fast thermoelasticity model, described in section 5.3.4. The peak electron blast force was recorded over a series of applied pulse durations using equation (29), ranging from 500 femtoseconds to 200 ps. The applied fluence in each case was kept constant, at the 500 fs threshold fluence of 0.32 J/cm^2.
Figure 5.17 Peak electron blast force versus pulse duration for 1030 nm laser pulses at a fixed applied fluence of 0.32 J/cm². The electron blast force rapidly decreases with increasing pulse duration.

The peak electron blast force shows a large dependence on the applied pulse duration, with a rapid decrease in value as the pulse duration is increased beyond 500 femtoseconds. The peak value rapidly goes to negligible values for pulse durations greater than 20 picoseconds. This is due to the large dependence of the electron temperature on the applied pulse duration, which decreases with increasing pulse durations. This is illustrated in which shows the simulated peak electron temperature in the ITO film as a function of laser pulse duration. In each case the applied fluence is kept constant at 0.18 J/cm².
As expected, as the pulse duration is increased, the peak electron temperature observed in the film decreases. A decrease of 27,000 – 7,000 K is simulated for an increasing pulse duration from 0.5 to 50 picoseconds.

5.4. ITO on PET thermal stress simulations

After laser irradiation of ITO films on PET, the induced crater on the film was shown to consist of fragmented and cracked edges, with no evidence of a melt ridge. This type of film removal process is often due to thermal stresses, which can develop under laser heating [194-196]. Using the finite element method, the temperature distribution in the ITO film on PET substrates can be simulated, after laser irradiation. This temperature rise in the material leads to material expansion, of which the magnitude is given by the thermal expansion coefficient. This leads to strain in the material, which can be defined as the fractional or percentage increase in the material length or volume. As the material expands, this can give rise to stress at various points in the material. A full description of the strain and stress methodology used in this study is given in section 2.7.2.
5.4.1. Temperature distribution in the ITO film and PET substrates using nanosecond pulses

Using the parameters defined in Table 10, for any given incident fluence the temperature profile in the ITO film and PET substrate can be found. The fluence region of interest is at the experimental threshold fluence, which was found to be 0.32 J/cm² and for ITO on PET and ITO on glass, using 355 nm nanosecond pulses. Figure 5.19 shows the simulated temperature profile in the film and substrate for a normalized $\omega_0$ spot radius of 0.5 µm. This is to better show the full region of interest at the film-substrate interface. The applied fluence is the respective threshold fluence for each film and substrate.

Figure 5.19. Peak temperature profile in the ITO film and PET/glass substrate for an incident pulse of spot radius 0.5 µm and applied fluence of 0.32 and 1.4 J/cm². The maximum temperature in the film is 990 K and 2000 K respectively.
For an incident pulse at the respective 355 nm threshold fluences of 0.32 and 1.3 J/cm², the peak temperature in the ITO film is approximately 990 K and 2000 K, for the ITO on PET and ITO on glass films respectively. Despite the threshold fluence being 4 times less for ITO on PET, the peak temperature in the ITO film is only twice less for the PET substrate. This is due to the direct absorption of the incident laser pulse in the PET substrate, as opposed to the negligible direct absorption in the glass substrate. The effect of laser wavelength of the peak film temperature is shown in Figure 5.20, at the respective film threshold fluences.

![Graph showing change in peak ITO film temperature with time for pulses at different wavelengths. The peak temperature for non-band to band pulses is much less than the ITO melting temperature. In the case of free carrier absorption wavelengths (>355 nm), the peak temperature in the film does not reach the ITO melting temperature. In the case of the direct transition wavelength, at 266 nm, the peak temperature in the film reaches 3000 K, the estimated ITO vaporisation temperature.](image)

The peak temperature in each case is 3000, 990, 1150, and 1170 K for 266, 355, 532 and 1064 nm respectively. In the case of free carrier absorption wavelengths (>355 nm), the peak temperature in the film does not reach the ITO melting temperature. In the case of the direct transition wavelength, at 266 nm, the peak temperature in the film reaches 3000 K, the estimated ITO vaporisation temperature.
5.4.2. Simulated strain and stress in the ITO film and PET substrate using nanosecond pulses

Due to the temperature increase in the film and substrate, material expansion takes place. The confined expansion of the materials will result in an associated strain, which normally has peak values at interfaces between two materials. The peak strain and stress was identified for ITO on PET using COMSOL, at the experimental threshold fluence temperature profile (0.32 J/cm²), shown in Figure 5.21. The strain theory was discussed in section 2.7.2, and its implementation in COMSOL was shown in section 3.6.2. The major tensile strain in this case is given as $\epsilon_{yy}$, the strain in the $y$ depth component of the substrate. The values of strain in the other tensors are negligible. The maximum peak strain occurs in the PET substrate, at the interface point between the film and substrate, centred at the peak of the Gaussian spatial profile. The maximum value of the associated expansive tensile stress occurs in the ITO film, at the interface between the film and substrate. The major stress tensor in terms of magnitude shown in Figure 5.21 is the $\sigma_{xx}$ tensor, the radial component along the film.
The overall evolution of the strain and stress follows the change in peak temperature of the film and substrate. The peak value of the strain, which is highest in the substrate, at the interface between the film and substrate was found to be 9.8%. The associated peak stress in the film was found to be 218 MPa. The strain and stress are distributed radially with profiles following the Gaussian intensity distribution of the laser. Due to the positive expansive stress generated in the centre portion of the film, the outside edge of the laser spot has a compressive stress, in this case peaking at -45 MPa.
5.5. Chapter Conclusions

In this chapter, the laser ablation properties of ITO on glass and ITO on PET were simulated using finite element methods, for nanosecond, picosecond and femtosecond laser sources. Some key properties of the thin film and substrate interaction were identified.

- **The simulated ablation properties of nanosecond pulses for ITO on glass can be described using the finite element heat equation**
  Nanosecond pulses at wavelengths of 355, 532 and 1064 show peak temperatures in the region of the ITO melting temperature ($T_m = 1900 \, K$), at the experimental applied threshold fluence. The crater diameters can be simulated using the radial distance where the simulated film temperature reaches the film melting temperature. Good agreement is noted between the simulated and experimental data.

- **The peak temperatures for the direct band gap 266 nm pulses reaches the ITO vaporisation temperature**
  The simulated ablation properties for 266 nm pulses differ compared to the non-direct bandgap pulses. The peak film temperature reaches the estimated ITO vaporisation temperature ($T_v = 3000 \, K$), at the experimental threshold fluence. The flux of vaporised particles away from the surface was found to be relevant only to 266 nm laser pulses. The crater diameter can be simulated using the radial distance where the simulated film temperature reaches the vaporisation temperature.

- **Heat conduction to the glass substrate plays a large for nanosecond laser pulses**
  Large amounts of heat are conducted across the interface region, during laser irradiation of the film with nanosecond pulses. The peak temperature of the glass substrate is equal to the film temperature in the interface region. However heat conduction alone cannot be used to predict the experimental substrate damage.
depth. Using the depth to which the conducted heat is greater than the glass vaporisation temperature under-estimates the glass damage.

- **The TTM model shows the evolution of the electron and lattice temperature on an ultrafast timescale in the ITO film**
  The peak lattice temperature for the ultrafast pulses does not reach the ITO melting for pulses below 0.71 J/cm². The TTM model predicts three regions which have a dependence on the applied fluence, a non-thermal region for applied fluence less than 0.71 J/cm², a melt region up to an applied fluence of 1.3 J/cm², and a vaporisation region at fluences greater than 1.3 J/cm². Using the radial melt distance to predict the crater diameter does not give a good agreement with the experimental crater diameters, indicating a potential non-thermal ablation mechanism for the ITO film on glass. In terms of heat conduction, picosecond and femtosecond laser pulses show much better heat localisation properties compared to nanosecond pulses. However, at the electron lattice coupling time, heat conduction to the substrate still takes place in a interface region of 5-10 nm.

- **Ultrafast lattice deformation takes place for femtosecond pulses at the experimental threshold fluence**
  The electron blast force was shown to have a peak value in the centre of the film, which reaches a peak value at a temporal time of \( t_0 + 590 fs \). The electron blast force then rapidly decreases, going to zero within 1 ps after laser irradiation, before the lattice begins to increase in temperature.

- **The thermal expansion of the PET under laser irradiation leads to strain and stress in the film and substrate**
  During laser irradiation, direct laser absorption by the PET, and heat conduction across the film interface to substrate, leads to temperatures in the substrate in the region of 900 K, at the 355 nm nanosecond threshold fluence. Due to the large coefficient of thermal expansion, this results in significant thermal expansion of the PET substrate at the interface. This thermal expansion leads to a strain in the substrate, as expansion takes place against the film. This strain is largest on the \( \epsilon_{yy} \) tensor, with a peak value of 9.8 % at the experimental threshold fluence. This
leads to an associated expansive stress in the film, which is largest on the $\sigma_{xx}$ stress tensor, with a peak value of 218 MPa.
Chapter 6

6. Discussion

In Chapter 6, the results of the previous two chapters are discussed. The experimental and computational results are used to explain various removal mechanisms for the film and substrate. The removal mechanism of the ITO film at nanosecond and ultrashort pulse durations, for both glass and PET substrates are presented, which are have not been covered in the current literature.

6.1. ITO film removal using nanosecond laser pulses

The surface topography of ITO on glass was examined for nanosecond pulses, across a range of parameters such as wavelength, spot overlap, pulse number, laser spot spatial distribution and laser spot radius. In this section the film removal is examined in terms of each of these parameters, using the experimental results and computational simulations.

6.1.1. ITO removal in the nanosecond time regime

After laser irradiation with nanosecond laser pulses with a photon energy below the ITO bandgap, the ITO craters show selective removal of the film from the substrate, with resolidified melt ridges (Figure 4.3). No evidence of ablated matter is noted in the ablation region. Film removal at fluences below the glass substrate damage threshold can be hypothesized as being a non-ablative heated melt flow process. The film and substrate are essentially a coupled system, and therefore the heating and removal of the film must also take into account the heating and removal of the glass substrate. As the laser energy is deposited in the film, the film is heated until it reaches the melting temperature ($T_m \approx 1900 \text{ } K$) (Figure 5.1). As the film thickness (20 nm), is much less than the laser absorption depth (500 nm @ 355 nm), the film is uniformly heated to the film substrate interface. A molten region will then develop at points where the surface temperature exceeds the melting temperature, and can overcome the material latent heat of melting.
The temperature profile of the molten region will be Gaussian, following the spatial Gaussian profile of the incident laser pulse. The surface tension $\gamma$ in the molten region varies with the local temperature $T$ given by equation (21). This variation in the surface tension gradient across the material, will cause the hot molten material to be driven to regions where the surface tension is lower, resulting in a theoretical radial fluid flow in the molten film. Re-solidification will take then place as heat diffusion drives heat into the substrate (Figure 5.3). Evidence of an exclusive film removal by melting is further shown in during imaging of the laser plasma using nanosecond laser pulses, in section 6.1. No observable plasma was detected using laser pulses which lead to selective removal of the film. Ejected material was only observed when the glass substrate was ablated at higher fluences. Examining the crater ridges in terms of conservation of material, it can be easily seen that the volume of material in the ridge does not equal the volume of material removed from the crater. Figure 6.1 shows an analysis of the ridge heights in terms of conservation of volume between the ridge and crater. The crater material volume was calculated and compared to the volume of the material re-solidified in the ridge.

![Graph showing ridge analysis](image)

**Figure 6.1** ITO crater edge after laser irradiation with a 355 nm nanosecond laser pulse, with an applied fluence of 1.4 J/cm²

Examining the crater ridge in terms of conservation of volume, when the film is selectively removed from the substrate, it appears that only a small fraction (7% @ $d = 9.5 \, \mu m$) of the molten material from the crater appears to be in the crater ridge itself. No evidence of re-deposited material can be seen, across all the non-direct transition wavelengths. If all the molten material was being deposited in the crater ridge, then at larger applied laser spot radii, which leads to larger craters, it would be expected that the
size of the ridge would increase. At larger spot radii over 20 µm and using tophat beam profiles, no crater ridges was observed. Therefore, molten material flow to the crater edges is only observed for large temperature gradients. Some other effect must be introduced which would explains this lack of conservation of film and ridge volume. Firstly, laser vaporisation can be ruled out as a film removal mechanism for laser pulses with photon energies below the ITO bandgap, as the peak temperature does not reach the ITO melting temperature (Figure 5.3) No re-deposited matter is observed experimentally in the crater, and this is confirmed by the peak temperatures observed in the heat diffusion model, which equal the ITO melting temperature at the threshold fluence. Examining the thermal model in section 5.1, absorption of the laser pulse by the conducting film, results in significant heat conduction to the glass substrate. In general, examining the temperature profiles in to the glass substrate at the 355 nm nanosecond threshold fluence (1.37 J/cm² @ ω₀ = 6.9 µm), the heat conducted to the substrate exceeds the soda lime glass melting temperature, to a depth of approximately 200 nm (Figure 5.8). This will result in a molten film and molten substrate, with a resulting interface boundary between the film and substrate now no longer a defined point. Diffusion of dopants from the film across the interface region may take place, moving indium and tin oxide atoms to the substrate. This has previously been noted for picosecond pulses at a wavelength of 583 nm applied to Ge films with thicknesses of 30 – 180 nm on Si substrates [197] After the laser pulse ends, cooling of the material now takes place, and re-solidification of the film and substrate takes place. This mechanism of material transfer to the glass substrate would explain the non-conservation of volume in the ridge, taking into account the lack of debris re-deposited during selective removal of the film from the substrate. This mechanism also explains the surface structure of ITO crater floor after laser irradiation, which has a grain structure similar to the film itself, much different from the expected glass amorphous structure (Figure 4.1).

As the photon energy of the laser pulses increases above the ITO bandgap, the properties of the surface topography and absorption change. The direct bandgap absorption of the 266 nm pulses leads to a much larger absorption coefficient in the film (Table 12). Examining the thermal model, high temperatures in the film are observed, 3000 K at the experimental threshold fluence. This results in a high recoil pressure in the film, which leads to a vaporised atomic flux away from the surface. The simulated data indicates a vaporisation process for film removal (Figure 5.2). This agrees with the change in surface
topography observed at 266 nm, where re-deposited material is observed, along with only minor re-solidified crater ridges (Figure 4.3). This vaporisation process leads to a challenge in terms of selective removal of the film from the substrate. Non-selective removal of the film is observed experimentally, with 5 nm of glass damage at the lowest applied fluence. This non-selective removal of the film is due to heat conduction across the interface to the substrate, which may be high enough to cause glass damage. Comparing the film-substrate interface temperatures, at the inter band transition wavelengths, the peak temperature is at the melt temperature ($T_m = 1900 \, K$), while for direct bandgap transitions the peak temperature is at the estimated vaporisation temperature, ($T_v = 3000 \, K$). As shown in the simulations, heat conduction takes place to the substrate, with high temperatures noted in the interface region between the film and glass (Figure 5.3). The vaporisation temperature of glass is in the region of $T_{vs} = 1800 \, K$. This shows the challenges in achieving selective removal of the film using 266 nm pulses, where the large difference in vaporisation temperatures between the film and substrate results in heat damage and non-selective removal of the film. Typically in the literature, selective removal of thin films on substrates are shown as possible due to the differences in threshold fluences between the film and substrate. Typically dielectrics are considered to have much larger threshold fluences than the film, and therefore this is the condition that makes selective removal possible.

In the case of multiple pulses, the crater surface topography shows new features compared to the case of a single pulse (Figure 4.17). In general, each successive pulse leaves a secondary re-solidified melt ridge around the crater, with an expanding crater diameter. However, no increase in the overall crater depth is observed. Each successive pulse appears to only interact with the “fresh” ITO outside the crater edge, resulting in a secondary smaller re-solidified melt ridge. Successive pulses do not interact with the preceding ridge, which leaves successive ridges in the material. This indicates that after material re-solidification, the ITO loses its absorption properties, and cannot undergo further phase change, as long as the laser fluence is not increased further.

6.1.2. Nanosecond ITO on glass trench formation mechanism

It was experimentally observed that a smoother film can be achieved by increasing the shots per area (Figure 4.14). In general, it is counter-intuitive that increasing pulse
overlaps result in less damage and smoother removal of the film. In general, for most bulk materials, increasing material damage occurs with increasing number of pulses and overlap, due to the lowering of the material threshold fluence with increasing pulse number [198, 199]. In the case of thin films, the process is more complicated, and the effect of SPA is dependent on the choice of material, and the removal mechanism of the film itself. High overlaps have been noted for picosecond smooth line removal of CIGs and Molybdenum films on glass [200], however in general in the literature no in-depth explanation for high overlap smooth removal is given.

In this study, the first laser pulse interacts with a fresh portion of ITO, with the film heats up under laser irradiation, if the applied fluence is high enough, the film will melt, resulting in fluid flow to the crater edge, and to the molten glass substrate. The time for second pulse to arrive depends on the laser repetition rate, which for the 355 nm laser pulses was at 20 kHz, resulting in a time between laser pulses of 50 µs, which is long enough for the heated material to return to the ambient room temperature. The second pulse will then interact with ITO crater already formed. Taking the example of an SPA of 2, results in the spatial peak of the second pulse at the crater edge, resulting in half of the spatial width of the pulse interacting with the glass crater floor, and other half interacting with the re-solidified crater edge and the next fresh portion of the ITO film. The portion of the pulse which interacts with the crater floor is increased, as a result the fluid flow for each consecutive pulse becomes smaller. Therefore, less material is available to re-solidify into a ridge, resulting in smaller ridge heights. The relationship between the ridge height and the SPA is shown in Figure 6.2. The data is taken from the results shown in Figure 4.14.
Initially, the ridge height reduces quickly, as initial changes in SPA (e.g. 1-5), result in large changes in how the intensity distribution overlaps. As the SPA is increased further, the change becomes less pronounced.
Comparing the lowering of the ridge height with SPA in Figure 6.2, and the variation in the normalised laser intensity with SPA in Figure 6.3 (c), a clear correlation between the two parameters can be seen. The height of the re-solidified ridge is directly dependent on the variation in the laser intensity along the line. As the SPA is initially increased from 1–5, a large change in both the ridge height is seen, due to the large change in the variation of the laser intensity across the profile. This begins to level out after 5 SPA, and only
minimal variation of laser intensity is seen after this point. In terms of optimisation of the laser process, there is a trade-off between the ridge height, and therefore smoothness of the laser line, and the processing time. As the SPA is increased, the laser processing time of a line will increase also, as for a fixed laser repetition rate, the marking speed of the galvanometer must be decreased to increase the SPA. This relationship is illustrated in Figure 6.4.

![Figure 6.4 Relationship between the overlap in shots per area, and the mark speed of the galvanometer, at a spot diameter of 40 µm, and a repetition rate of 20 kHz](image-url)

This results a trade-off between the ITO line removal smoothness, and the overall processing time.

### 6.1.3. Threshold fluence for ITO on glass

Experimental results show a near linear dependence between the threshold fluence and the applied spot radius in the tested range. For the 355 nm results shown in Figure 4.23, as the spot radius increases from 6.4 to 21.6 µm, a 3.38 fold increase, the threshold fluence decreases from 1.52 to 0.42 J/cm², a 3.61 fold decrease. The relationship is essentially linear in the tested range. At a wavelength of 266 nm, as the spot size is increased from 5.54 to 19.49 µm, a 3.51 fold increase, the threshold decreases from 0.90 to 0.33 J/cm², a 2.73 fold decrease. Using the tilted plane method to determine the threshold fluence shows good accuracy within the experimental error, when compared to the standard horizontal focussed method. At a spot size of 5.54 µm at a wavelength of 266 nm, the
focussed threshold is 0.83 ± 0.09 J/cm², compared to the tilted plane result of 0.90 ± 0.03 μm. Discrepancies in the two threshold fluence values may be due to small changes in the reflectivity of the sample with the angle of incidence. The inclined plane is set at a 1:10 gradient, which gives an angle of incidence of 5.7°. Assuming a refractive index of ITO in the UV of 2.2, the change in reflectivity from 0 to 5.7° will be approximately 0.10 to 0.14. This will cause the tilted threshold values to increase compared to those obtained using the horizontal at-focus method. Using these reflectivity values gives corrected absorbed threshold fluences of 0.75 ± 0.08 J/cm² for the focussed threshold, and 0.77 ± 0.2 J/cm² for the tilted threshold.

The NA of laser system can also modify the threshold fluence, as seen in Figure 4.22. As the film is heated under the incident laser pulse, the film may reach the melting point. If the fluence is sufficiently high enough, the glass substrate can be damaged. This leads to large amounts of debris re-deposited in the crater area. Interaction between the material ejection and the later part of the laser pulse, can lead to shielding of the incident pulse, through processes such as Inverse Bremsstrahlung, photo ionization [201] and Mie Absorption [202]. The degree of shielding will depend on what portion of the incident pulse falls within the region of the plume. The NA defines the propagation of the laser pulse towards the material surface, as seen in (6). The spatial width of the laser pulse above the material, and therefore the region of the incident pulse which falls within the expanding plume, will be determined by the NA.

Examining the threshold fluences in terms of the absorbed threshold fluence, shows that 266 nm pulses have the largest energy requirement for removal of the film, almost five times the magnitude noted at the wavelengths where free carrier transitions dominate (Table 15). The lowest absorbed threshold fluence occurs at the lowest energy photon, at 1.2 eV (1064 nm). In free carrier absorption, in order for the free carrier electron to absorb the incident photon, momentum conservation with optical and acoustic phonons must occur. This typically gives an absorption coefficient $\alpha \sim \lambda^2$. The lower photon energy of 1.2 eV (1064 nm), will allow a more efficient absorption of the incident photon, compared to 532 nm. Following this logic to 355 nm (3.5 eV), we might expect the absorbed threshold to the higher again, as the higher energy photon should have a less efficient absorption free carrier absorption than the 532 nm photon, however only a minor increase in the absorbed threshold fluence is noted (Table 15). In order to explain this, the bandgap under heated film conditions must be examined. The bandgap of semiconductors in
general, decreases with increasing lattice temperature [203], approximately going as
\[ E_g(T) = E_o - \left[\alpha T^2 / (T + \beta)\right], \]
where \( \alpha \) and \( \beta \) are fitting parameters dependent on the material. This decrease in the bandgap with increasing temperature, may result in a direct transition for the 355 nm (3.5 eV) pulses for a limited time, if the lattice temperature increases enough so that the bandgap decreases by 0.5 eV. This direct transition will increase absorption in the film, resulting in a lower than predicted absorbed threshold fluence, which lies outside the \( \alpha \sim \lambda^2 \) regime expected for free carrier absorption.

The dependence of the absorbed threshold fluence on photon energy for ultrashort pulses shows an increase with increasing photon energy in the tested range, for both femtosecond and picosecond. This increase agrees with the \( \alpha \sim \lambda^2 \) regime expected for free carrier absorption. No influence from the lattice temperature is observed, as the ultrashort laser pulse interacts with a thermally cold lattice for the majority of the time taken for laser energy deposition.

### 6.1.4. Threshold fluence dependence on spot radius

To investigate the dependence of the threshold fluence on the spot radius, the gradient of the fluence in the thin film is considered. The absolute value of the fluence gradient \( |\frac{\partial \phi(r)}{\partial r}| \) for the incident pulse varies inversely with the square of the incident spot radius.

\[
\left| \frac{\partial \phi(r)}{\partial r} \right| = \frac{-4r}{\omega_0^2} \frac{\phi_0 e^{-2r^2/\omega_0^2}}{\omega_0^2} \tag{44}
\]

The calculated fluence gradient for various spot radii across the material surface for a normalised pulse with a peak fluence \( \phi_0 = 1 \). The peak values of the fluence gradient can be found by solving equation (9) for \( \frac{\partial^2 \phi}{\partial r^2} = 0 \).

\[
\frac{\partial^2 \phi}{\partial r^2} = \frac{4}{\omega_0^2} \phi_0 e^{-2r^2/\omega_0^2} \left[ \frac{4r^2}{\omega_0^2} - 1 \right] \tag{45}
\]
The peak values in the fluence gradient are fitted to $A (1/r) \exp(2)$, $A$ is a fitting value given as 0.082. In general, the change in fluence gradient and threshold fluence show a clear defined link, in terms of variation with respect to the applied spot radius.

Figure 6.5 Change in the laser fluence gradient with spot radius. The lower graph shows the fit of the peak values with the Lorentzian fit determined from the COMSOL absorption model.

This occurs at values of $\pm \omega_0/2$. The maximum values of the fluence gradient, for different values of $\omega_0$, are plotted against their position in part (b). The main variation of the fluence gradient is up to values of $\omega_0/2 = 14 \mu m$, giving an $\omega_0$ spot radius of 28 $\mu m$. After spot radii of 28 $\mu m$, the change in the maximum fluence gradient is minimal. Figure 6.6 shows the computationally determined absorption coefficients over a range of spot radii, in order for the film to reach the melting temperature, at the experimentally
determined threshold fluence, taken from Figure 6.5. The absorption coefficient trend, plotted as $1/\alpha$, is fitted with the $(1/r) \exp(2)$ fit, shown in Figure 6.6. As the spot radius is increased, the simulated absorption coefficient of the film must be increased in order to reach the experimentally determined threshold fluence.

![Graph showing simulated change in absorption coefficient](image)

Figure 6.6 Simulated change in $\alpha$, plotted as $1/\alpha$, fitted with the curve taken from the change in peak fluence gradient

The relationship between $\alpha$ and $\partial \phi / \partial r$ is established again through the finite element heating model. The simulated change in the absorption coefficient shows the same Lorentzian trend, as the calculated change in the fluence gradient, as the spot radius is increased. Both computationally and analytically, the absorption coefficient for an ITO thin film, is shown to vary with $\partial T / \partial r$, and hence $\partial \phi / \partial r$. This leads to an inverse relationship between the measured laser threshold fluence and the laser absorption coefficient, defined by the applied laser spot radius.

Using pulses in the nanosecond time regime, results in interactions between the laser pulse and a heated film. The temperature gradient in the film is defined by the gradient of the applied fluence. Parts of the pulse may experience modified absorption characteristics due to the increased temperature of the material. Laser absorption by materials is mainly associated with the electronic properties of the material. The absorbed component of the incident laser intensity into the material is given by $I(y) = aI_0 \exp(-\alpha y)$. The absorption coefficient $\alpha$, is related to the imaginary part of the complex refractive index through $\alpha =$
As discussed earlier, ITO has a large free electron density with a Fermi level at the bottom of the conduction band, and a band gap of approximately 3.8-4 eV [204]. The absorption of laser energy is through both inter-band absorption, where an electron is promoted from the valence to the conduction band, or through intraband absorption by the large density of free electrons. The absorption by free carriers can then be written in terms of the Drude model [75]. This gives an absorption coefficient which is proportional to $\lambda^2$ and $n$, the density of free electrons.

The absorption coefficient in the film, is therefore directly dependent on the density of the free electrons in the absorption area. This has been shown previously for ITO films, where the relationship between carrier concentration and absorption coefficient is essentially linear, where the carrier concentration changes through increasing the film thickness [14]. As the electrons absorb energy, they will move through the lattice due to the applied electric field, known as a conduction current, or due to a concentration gradient, known as the diffusion current. The electrons can then scatter through electron-electron scattering, grain boundary scattering [205] and impurity scattering [206]. Impurity scattering is the dominant process in ITO films [15]. Electronic diffusion in semiconductors is typically defined through a current density $J_n$ (A cm$^{-2}$). Assuming a temperature gradient $\partial T/\partial r$, the current density $J_n$ can be defined using three terms as

$$J_n = \frac{qn\mu_n E}{\text{carrier conduction}} + \frac{qD_n \partial n}{\text{carrier gradient}} + \frac{qD^T_n \partial T}{\text{temperature gradient}}$$  \hspace{1cm} (46)$$

where $q$ is the electronic charge, $n$ is the density of free carriers, $E$ is the applied electric field, $\mu_n$ is the mobility, $D_n$ is the diffusivity defined by the mobility, $\partial n/\partial r$ is the gradient of free carriers and $D^T_n$ is thermal diffusion coefficient (or Soret coefficient) given as $\mu_n kn/q$. The first term describes conduction of carriers under an electric field, the second term describes diffusion of carriers due to a carrier gradient, and the third term describes diffusion of carriers under the applied temperature gradient. The change in the density of free electronic carriers $n$, is proportional to the current density. As seen in equation (46), the current density $J_n$ away from the laser absorption area is directly proportional to both $\partial n/\partial r$ and $\partial T/\partial r$, which are defined by the gradient of the applied fluence $\partial \phi/\partial r$. This is determined by the laser spot radius $\omega_0$. As energy is absorbed by the electrons in the excitation area, the rate of absorption during the incident pulse will
decrease with time for all spot radii, as \( J_n \) drives a portion of the electronic density \( n \) away from the absorption area. The rate of decrease of the absorption will therefore be determined by the magnitude of \( J_n \) itself, which can vary with the laser spot size conditions. As \( \omega_0 \) is increased from its initial value, \( \partial \phi / \partial r \) will decrease proportionally, which will lead to a decrease in both \( \partial n / \partial r \) and \( \partial T / \partial r \). This is will have an overall effect of decreasing the magnitude of \( J_n \) away from the excitation area during the laser pulse, relative to smaller spot radii. If the density of electrons in the excitation area is higher overall during the pulse, the threshold fluence will be lower, as more absorbers are available to thermalise the incident energy to the lattice and enable it to reach the melting temperature. This leads to the conclusion that for ITO thin films, the overall averaged laser absorption coefficient \( \alpha \) over the duration of the nanosecond pulse, can be said to be directly proportional to \( \partial \phi / \partial r \) and \( \partial T / \partial r \) in the material, and therefore the spot radius \( \omega_0 \).

As the pulse duration is decreased into the ultrashort time regime, the experimental change in threshold fluence with spot radius, shows the opposite result when compared to nanosecond pulses (Figure 4.24). The threshold fluence for ultrashort pulses increases in the tested applied spot radius range. Again, following from the nanosecond spot radius analysis, the electronic diffusion during the laser pulse must be examined

As established by the two temperature model [80], energy is first deposited in the electronic subsystem, where an electron temperature \( T_e \) is established within 5 – 10 fs. The thermalisation time for electrons with optical phonons is typically around 2 – 10 ps. The incident laser pulse, in the case of ultrashort pulses, therefore interacts with a cold lattice, and the absorption is through the electronic subsystem. Examining equation (46), at ultrashort pulse durations, \( \partial T_L / \partial r \) has not been established during the pulse, and the current density away from the pulse area is dominated by the electronic diffusion term. Ballistic electrons also play a role in electronic motion under high intensity fs pulses [207]. As the electronic subsystem absorbs the incident pulse, \( T_e \) will be many magnitudes greater than \( T_L \). As discussed in [208], the band gap in the material \( E_{cv} \), can be described in terms of free energy

\[
\Delta E_{cv} = \Delta H_{cv} - \partial T_e / \partial r \Delta S_{cv} \quad (47)
\]
Where $\Delta H_{cv}$ and $\Delta S_{cv}$ are the enthalpy and standard entropy of the excitation of standard carriers across the bandgap. Gradients in $T_e$, defined as $\partial T_e/\partial r$, are determined by the fluence gradient in the material, set by the spot radius $\omega_0$. $\partial T_e/\partial r$ defines the gradient in bandgap $\Delta E_{cv}$. The bandgap will be smallest where the electrons are the densest and hottest. This gradient in the bandgap has an effect of an internal field, which drives the carrier density $n$, to regions where the bandgap is minimal. This acts to oppose the outward electronic diffusion, and acts as an electronic plasma confining effect. The magnitude of the confinement is then determined by the gradient in $\partial T_e/\partial r$. As $\omega_0$ is decreased, the gradient in $\partial T_e/\partial r$ and therefore $\Delta E_{cv}$ increases. This causes the electronic confinement effect to increase with decreasing spot radius. Larger numbers of electrons stay confined in the film absorption area as $\omega_0$ is decreased, which will lead to greater thermalisation of the incident laser energy into the film. This will cause the threshold fluence to lower accordingly with decreasing spot size. This theoretical formulation agrees with the experimental observed trend in the ultrashort threshold fluence (Figure 4.24).

6.1.5. Substrate glass damage using nanosecond laser pulses

As the applied fluence is increased, the film will reach the threshold fluence, with complete removal of the film takes around this point (Figure 4.3). A linear increase in glass damage with applied fluence is then observed. Comparing nanosecond and femtosecond pulses, glass damage is more prevalent at nanosecond pulse durations, with large amounts of ejected material visible at thresholds just above the threshold fluence (Figure 4.30). In general, in order for direct glass ablation to take place using nanosecond pulses, very high applied fluences are required, typically over 50 J/cm². This is due to the low intensity of the nanosecond laser pulse, which is much lower than that required to generate the non-linear absorption process such as avalanche and multiphoton ionisation, which are critical to the dielectric removal process. Examining the glass damage onset for 355 nm nanosecond pulses, damage is noted at around 1.5 J/cm², which is over 30 times lower than that observed for raw glass. This damage to the glass substrate is a much reviewed issue in the literature [209-211]. In general, the mechanism for dielectric substrates is not known, however it is generally considered to be due to heat conduction across the thin film substrate interface. While heat conduction across the interface does
play a large role in the glass damage process, it is proposed to be only partially responsible for glass damage.

Damage to the glass substrate was simulated using the finite element model, and compared to the experimental glass damage observed Figure 5.9. Using heat conduction as the primary method of glass damage, results in an under-estimation amount of glass damage to the substrate. Also, if glass damage is due to heat conduction alone, then there should be an upper limit on the depth to which the glass can be damaged. In order for the glass damage to linearly increase in the moderate fluence range, the temperature in the film must also increase to compensate this. However, there is a maximum temperature at which the film can be heated, as once the vaporisation temperature is reached, material removal via plasma and plume ejection will take place. This upper limit on glass damage is not seen experimentally, with a steady fixed linear increase observed. Secondly, if glass damage was solely due to heat conduction, then the linear increase in glass damage should be independent of the applied wavelength, once the values have been normalised with the respective wavelengths threshold fluence. However as observed experimentally, the increase in glass damage shows a dependence on the applied wavelength (. 532 nm photons show the most effective damage to the glass substrate, followed by 355 and 1064 nm, with 266 nm photons showing the least effective damage.

In order to explain the experimental and simulated results, another model of glass damage is proposed. In this model, damage to the substrate is explained as being through heat conduction to the substrate, which induces dielectric absorption of the later part nanosecond pulse. In order to illustrate this, Figure 6.7 shows the temperature rise in the glass substrate at the depth of 10 nm, compared to the temporal overlap of the nanosecond laser pulse.
Figure 6.7 Peak temperature in glass substrate at a depth of 10 nm, at the nanosecond 355 nm threshold fluence of 1.3 J/cm². The right hand axis shows the normalised intensity profile of the applied laser pulse.

As heat is conducted across the interface, the glass substrate begins to heat up to high temperatures. This leads to an interaction between the later part of the nanosecond pulse and a heated dielectric substrate, and for the interface portion of the substrate, a potentially molten region. Therefore, the glass dielectric absorption coefficient, which is normally low \( (1 \times 10^4 m^{-1}) \), may change due to the altered conditions caused by heat conduction.

The effects of glass under high heat can lead to a number of processes which may lead to an increase in the absorption coefficient. The chemical composition of soda lime contains many dopants, however the dominant molecule is silicon dioxide \((SiO_2)\), therefore for simplicity defect creation and absorption is going to be only taken into account on the \( SiO_2 \) molecule. In general, the temperature dependent density of defects \( n_t \) in materials exhibits Arrhenius behaviour [212].

\[
n_t = n_0 e^{\frac{-E_f}{kT}}
\]  

(48)

Where \( n_0 \) is the initial defect population, \( E_f \) is the formation energy of the defect center, \( k \) is Boltzmann’s constant and \( T \) is the material temperature. The laser absorption is
dependent on the glass defect concentration, giving a laser defect absorption coefficient $\alpha_d$

$$\alpha_d = \alpha_0 \exp \left( \frac{-E_f}{kT} \right)$$ (49)

Where $\alpha_0$ is the defect centre absorption coefficient, $E_f$ is the defect creation energy given by the Si-0 bond of 3.5 eV [213]. In order for absorption in the glass to take place, significant free electrons must be available in the conduction band to absorb the laser energy, which will cause the dielectric properties to change from that of an insulator towards that of a metal. The source of the conduction band electrons is through non-linear absorption properties of dielectric during femtosecond and picosecond laser pulses, described fully in section 2.7.1. At the low fluences used in this study, the non-linear absorption properties of the nanosecond pulses are negligible. Therefore, a secondary source of conduction band electrons is needed, in order for induced absorption to take place.

ITO as an n-type transparent direct band gap semiconductor has a low ablation threshold and a high electrical conductivity. Excess free electrons are provided by the dopants in the film and the electron density is up to $10^{21} cm^{-2}$. Generating free electrons in the ITO film can be achieved with very low ablation energies. When the incident laser pulse transfers energy to the ITO electrons, they can scatter and diffuse throughout the film. For gold films, electrons ballistically scatter and diffuse at the Fermi velocity, with electrons travelling 10 nm in approximately 100 fs [214]. During laser irradiation using nanosecond pulses, due to the very thin nature of the film, it is possible that electrons will diffuse across the thin film interface to the substrate. Once the electrons are in the substrate, free carrier absorption in the dielectric can occur. Predicting the exact density of free carriers that will diffuse to substrate is challenging, due to temporal nature of laser pulse, and the exact relationship between the electronic diffusion length and scattering at grain boundaries and impurity sites, as well as the interface itself. However, we can describe a generalised induced absorption coefficient in the substrate which goes as
\[ \alpha_{\text{glass}}(T, n, x, y, t) = \alpha_g + \alpha_0 \exp \left( \frac{-E_f}{kT(x, y, t)} \right) + \frac{\omega_p^2 v_e}{c(\omega^2 + v_e^2)} \]  

Where \( n(x, y, t) \) is the space and time dependent density of electrons which will diffuse across the interface into the glass substrate. The first term on the right \( \alpha_g \) is the absorption coefficient of glass, in the UV typically given as \( 1 \times 10^4 m^{-1} \), the second term describes the absorption increase in the glass due to the generation of defects, due to the temperature from heat conduction to the substrate, and the third term describes absorption in the glass due to free carrier absorption from electrons diffusing across the interface. These two added terms will result in an increase in the absorption coefficient for the glass substrate, which will lead to higher temperatures in the glass substrate. This will increase the level of damage in the substrate, which may explain the discrepancies noted between the experimental and simulated values for the ablation depth.

6.2. Threshold fluence dependence on pulse duration and wavelength

The threshold fluence for 20 nm ITO on glass, has been calculated in the previous sections. The three main wavelengths were 343/355, 515/532 and 1030/1064 nm. The pulse durations used were in the nanosecond, picosecond and femtosecond time regime. Figure 6.8 shows the overall applied threshold fluence dependence calculated for 20 nm ITO on glass, as a function of wavelength and pulse duration. The pulse duration is plotted on log scale.
A number of trends in the data can be observed. Firstly overall, decreasing the pulse duration leads to lower threshold fluences, across all the tested wavelengths. In general, this is expected due to better heat confinement in the thin film, and increased absorption due to non-linear effects in the film, at ultrafast pulse durations. Overall, comparing the trend across the wavelengths, as the pulse duration is decreased, the gap between wavelengths becomes less pronounced overall. In the nanosecond time regime, the green wavelength has a threshold fluence almost 7 times the UV threshold fluence. In the picosecond time regime, this decreases to a factor of 4.5. In the femtosecond time regime, the difference decreases further to a factor of 3. It becomes clear from this, that differences in the threshold fluence across the wavelengths are highly dependent on the pulse duration. At pulse durations in the nanosecond time regime, where the thermal nature of the pulse material interaction dominates, the gap in threshold fluences is largest. At ultrafast pulse durations, where the thermal interaction of the pulse and the material is minimized, the gap between the threshold fluence decreases across the wavelengths.

6.3. ITO on PET film removal

The effect of the substrate on the ablation properties of the film was examined through laser interaction experiments on ITO on glass, and ITO on PET. The overall ablation properties of both systems varied in terms of a number of properties, such as applied
threshold fluence, crater surface topography, plasma emission, simulated peak temperature, and generated stress in the film during laser heating. Firstly, in terms of the film threshold fluence, the comparative trend for both systems is shown across the range of wavelengths used, as seen in Figure 6.9.

![Graph of threshold fluence vs. wavelength](image)

Figure 6.9 Calculated threshold fluence for ITO on glass and ITO on PET, for wavelengths of 266, 355 and 532 nm. The threshold for ITO on PET is lower compared to ITO on glass across all of the wavelengths tested.

Overall, ITO on PET has a lower threshold fluence across all the applied wavelengths. The fractional decrease in the threshold fluence from glass to PET is 2.1, 4.2, 1.3 and 3.8, for wavelengths of 266, 355, 532 and 1064 nm. Starting with computational simulations, after laser irradiation, the peak temperature in the ITO film on PET substrates does not reach the melting temperature after laser irradiation at the threshold fluence, with a peak temperature below the threshold fluence by almost 1000 K (Figure 5.20). This clearly indicates that the film removal process for ITO on PET is not driven by thermal methods. This non thermal removal process is further observed in the crater surface topography (Figure 4.32). A fractured cracked crater edge with no evidence of thermal melting or vaporisation, is observed at all pulse durations and wavelengths. This observed method of potential non thermal removal led to the examination of the strain and stress in the film and substrate during laser irradiation. Examining the strain and stress using finite element simulations, shows significant thermal expansions of the PET under laser heating, due to both direct absorption by the PET, and due to heat conduction across the film substrate interface (Figure 5.21). This is in contrast to ITO on glass, where no direct absorption in
the dielectric takes place. This thermal expansion of the PET substrate leads to significant strain at the interface, with a magnitude of approximately 10%. This strain leads to an associated expansive stress in the film, with a magnitude of 240 MPa at the threshold fluence, examined for 355 nm laser pulses. This stress generated at the interface must clearly able to overcome the adhesive strength to the film, which results in thermo-elastic delamination of the film. This de-lamination film removal effect results in the characteristic fragmented edge observed at all wavelengths and pulse durations. This also explains the lower threshold fluence shown across the range of laser wavelengths, and the lack of ejected plasma during nanosecond laser ablation of ITO on PET film (Figure 4.50). However at ultrashort pulse durations, the wavelength plays a much more observable role. Extensive damage to the PET substrate was obtained using UV femtosecond pulses (Figure 4.37), along circular ripples structures which were dependent on the applied wavelength. Much cleaner removal of the film was obtained using IR femtosecond pulses (Figure 4.38). Femtosecond pulses can result in very localised heat in the thin film structure, which allows a much cleaner delamination process. However if the substrate is too highly absorbing, as seen here for UV pulses, extensive substrate damage can be induced.

Nanosecond film removal of ITO can therefore be separated into two regimes. A thermal film removal process for glass substrates with low thermal expansion characteristics, and a thermo-elastic delamination process for flexible substrates with high thermal expansion characteristic. However, in terms of the application of laser pulses for selective removal of ITO from flexible substrates, there are many remaining challenges. Due to thermos-elastic ablation process, the fragmented edges can result in a removal process which is not suitable for display devices, due to the high line visibility of the edge. Current laser systems in the nanosecond and ultrashort time regime do not seem to currently have the capability to produce an optimal film removal process for TCO’s on flexible substrates.

6.4. Ultrashort ITO thin film removal method

The ablation of materials using femtosecond laser pulses can consist of a variety of physical ablation mechanisms, including stress effects, phase explosion, spallation, Coulomb explosion, and ultrafast lattice deformation. Determining the removal method of the ITO film using ultrashort laser pulses is therefore challenging. Any proposed
mechanisms must be able to explain the observed surface topography along with results of the TTM model.

6.4.1. Ultrashort laser interaction for ITO on glass

The main focus of this discussion will focus on ablation properties and mechanisms of ITO film removal using picosecond and femtosecond laser pulses.

Overall, the key factor in the determination of the surface features was the applied fluence. The overall ablation process in terms of surface topography, was generally homogenous for the picosecond and femtosecond pulse used in this study, and across the range of wavelengths used (Figure 4.9).

The surface topography of the ultrashort ITO craters shows a number of characteristic features. Film removal at low applied fluence (< 1J/cm²) leads to incomplete removal of the film, in general with a total depth of 10 nm, a cracked fragmented crater edge, and the generation of nanoparticles with a narrow distribution with diameters on the order of the film grain size (Figure 4.13). At higher applied fluences (> 1 J/cm²), selective removal of the film is observed, again consisting of a cracked crate edge and re-deposited nanoparticles, with no thermal features identified (Figure 4.9). At larger applied fluences (>1.4 J/cm²), minor damage to the substrate is observed, with a depth of 5 – 10 nm. This damaged ablation region, results in the smoothest overall film removal appearance. This type of smooth removal leads to challenges in the determination of the selective removal point of the film. Visually, what might be considered the best cleanest removal of the film, may actually be due to minor damage of the substrate, which is only visible through in-depth analysis of the crater itself.

Comparing the surface topography results to the simulated TTM, a non-thermal ablation regime is predicted from the peak lattice temperatures for low applied fluences (< 0.7 J/cm²), with a melt region up to 1.1 J/cm², followed by film removal via vaporisation at higher applied fluences. However experimentally, no melt or vaporisation regions are observed on the film crater surface. The TTM model does predict a large electron blast force, which occurs during ultrafast laser pulse absorption, which acts as a deformation force on a thermally cold lattice. The magnitude of this electron blast force is highly dependent on the applied pulse duration, which significant peak values observed for pulse durations less than the observed electron phonon coupling time (≈ 20 ps). Experimentally
in this case, the laser pulse durations are less than this characteristic time, \((\tau = 500 \text{ fs}, 10 \text{ ps})\). This signifies that a potential non thermal lattice deformation acts on the ITO film before lattice thermalisation can take place. The lattice deformation in this case would act on areas which are weakest in the film structure, in this case at the grain boundaries. Breakup of the film at the grain boundaries would result in re-deposited nanoparticles on the order of the film grain size, which is observed experimentally in this study. This ejection of material also takes place before lattice thermalisation takes place, or before film melting occurs. This explains the angular appearance of the re-deposited nanoparticles. The appearance of spherical nanoparticles indicates film melting takes place before ejection. Spherical nanoparticles were only observed at 343 nm femtosecond laser pulses, which indicated that film melting may have taken place before material ejection. This may be due to higher absorption coefficient of laser pulse in ITO in the UV. Overall, the ultrafast deposition of laser energy leads to a number of competing processes. The rapid absorption of laser energy by the electron sub-system generates a non-thermal stress in the film, which results in lattice de-formation. The electrons then couple their energy to the lattice, which results in thermal heating of the film on a picosecond time scale. Heat conduction from the film to the substrate then begins to occur. This heat conduction is relevant in this study due to the very thin nature of the film. Generally, in the literature, heat conduction effects with ultrashort pulses are ignored. However, as shown in this study, heat conduction can take place to the substrate within picoseconds, which can result in significant glass temperatures. This explains the thin layer of glass damage observed experimentally, at moderate fluences. Typically ultrashort pulses are considered greatly superior in terms of the ablation removal properties of thin films. However as shown in this study, ultrashort pulses can lead many suboptimal features on very thin ITO films, including fragmented edges with a high ridge height, glass damage, incomplete removal of the film, and re-deposited debris. These non-optimal features are due to essentially non thermal removal of the film, caused by fragmentation of the grain boundaries. However when ultrashort pulses are used to create an overlap (Figure 4.15), the resulting crater shows a much cleaner removal than compared to nanosecond pulses, where the thermal melting process of the pulses results in significant re-solidified crater ridges. The ultrafast grain breakup of the film allows smooth removal of a line at low SPA.
The peak electron blast force was shown to be highly dependent on the applied pulse duration. The peak force in the film was found to drop off sharply as the pulse duration was increased towards the electron-phonon coupling time. The peak electron blast force was found to be negligible for pulse durations greater than 20 picoseconds. Therefore it can be hypothesised that the non thermal grain breakup mechanism is only valid for laser pulses with a pulse duration less than 20 picoseconds. It can be proposed that therefore laser pulses greater than this will lead to a thermal film removal process. The exact mechanism of this ultrashort thermal process may be through a number of methods, including vaporisation, phase explosion of normal boiling. This leads to the definition of the optimum thermal film removal process of the ITO film, must be for laser pulse durations roughly in the region of 20-50 picoseconds. This will result in a thermal film removal process, however due to the minimised pulse duration, the heat diffusion length will be small, resulting in heat conduction to the substrate which will be greatly reduced compared to the standard nanosecond pulses used in this study. This region of the pulse duration spectrum (20-500 ps) is vastly under studied in the literature, with most studies concentrating on the < 10 ps range. It is proposed here that the optimal process for very thin ITO films may be in the pulse duration region above this. An in-depth study of the effect of pulse duration in this mid-ultrashort region is needed to confirm this hypothesis. However here we can define a film removal mechanism which is directly related to the electron phonon coupling time. For pulses with \( \tau_p < \tau_{ph} \), film removal via non thermal pathways will take place, and for pulses with \( \tau_p > \tau_{ph} \), film removal will take place via thermal methods.

As well as the film removal being dependent on the relationship between the pulse duration and the electron phonon coupling time, film removal may also be dependent on the thickness of the film. This study only examined ITO films with a thickness of 20 nm. However as observed in literature, most studies undertaken on ITO on glass have been with film thickness > 100 nm. However as the electron blast force is dependent on the gradient of the electron temperature into the film, the value of the blast force will vary depending on the thickness of the film. The variation in \( T_e \) with depth will depend on the laser absorption coefficient, with absorption depths given as \( 1/\alpha \). This gives absorption depths in the ITO film for wavelengths of 266, 355, 532 and 1064 nm of 33, 333,1100 and 833 nm respectively. This gives large absorption depths in case of all non-direct bandgap wavelengths. However in practice it is unlikely that films around these thickness
would result in a non-thermal ejection process. As described earlier, in order for electron
blast non thermal ejection to take place, grain breakup must occur before energy
thermalisation. For larger thickness films, it is unlikely that there would be time for the
deeper grains in the film to be ejected before thermalisation would take place. While they
would experience a deformation force, it is likely that melting or vaporisation would take
place for larger films. Therefore the electron blast force is only suitable for very thin
films, in this case in the region of 20 nm. A detailed study on the effect of film thickness
on the ultrashort ITO removal mechanism would likely reveal a transition from complete
non thermal film removal to thermal mechanisms as the film thickness was increased.
Chapter 7

7. Conclusions and future work

This work has focussed primarily on the laser interaction of short and ultrashort laser pulses with thin ITO films. The main goal of the research was to identify the film removal methods for a number of key parameters, such as wavelength, pulse duration, applied fluence, laser spot overlap, substrate material and laser spatial intensity profile. The research was motivated by the general lack of in-depth research in the literature, on the removal properties of thin TCO films.

The laser film irradiation was characterised using a number of methods. The surface topography was analysed using AFM, which allowed in depth analysis of the ablation process. The laser film interaction was also simulated finite element methods, which allowed key parameters during laser irradiation such as temperature, strain and stress to be examined. The ablation process for thin ITO films can be spilt into a number of groups, depending mainly on the laser wavelength, pulse duration and substrate.

Firstly, the removal for ITO on glass is discussed. Film removal using nanosecond pulses can in general be classified as a thermal removal process. Laser pulses with a photon energy below the ITO bandgap result in film removal through heated melt flow, with no removal through ablative means. Laser pulses with a direct bandgap transition result in ITO ablation through vaporisation. This thermal process leads to heat conduction across the film substrate interface, which can result in damage to the glass substrate. As the pulse duration is decreased to the ultrafast time regime, film removal is hypothesised as taking place predominately through ultrafast film lattice deformation induced by the hot electronic subsystem, resulting in a non-thermal grain breakup. This film removal mechanism results in superior line trench quality at low SPA’s compared to nanosecond laser pulses.

The choice of substrate for film deposition was found to have an impact on the film removal process. Film removal for ITO on PET substrates for all tested laser pulses, using both nanosecond and ultrashort laser sources, was found to be through thermo-elastic delamination. The expansive stress generated at the interface between the film and
substrate, leads to large stress in the film. This large stress can then overcome the film adhesion strength, resulting in delamination of the film away from the substrate.

The fabrication of custom silicon spatial beam shaping elements allowed the effect of the spatial beam profile on the laser ablation properties of the film to be examined. Tophat beam profiles result in an optimised film removal for ITO, using nanosecond laser pulses. Due to the flat nature of the intensity profile, no fluid flow takes place during the melting of the film. This results in a minimised re-solidified crater edge, which reduces line visibility.

7.1. Future work

In this work, further insight into some of the film removal methods and simulations, could lead to greater control of film removal process, along with an increased understanding of the exact mechanisms.

In the nanosecond time regime, the exact nature of the fluid flow during laser irradiation is still unclear. The interaction of the molten film and molten substrate is a key area of interest. Fluid dynamics studies, done in real time conjunction with the heat equation, would allow the exact fluid flow process to be characterised. This would allow the exact mixing nature of the molten film and substrate to be found, and the dependence on the temperature gradient in this process. A second area which would benefit from a more in-depth analysis would be the simulation of the increase in absorption of the glass substrate during nanosecond laser irradiation. In this study, heat conduction is shown to be responsible for glass damage at the interface, however, glass damage is primarily an induced direct absorption effect, due to defects and electron diffusion from the film. It would be possible to break down the absorption coefficient of the glass into the various components, taking into account the temperature dependence of each. Integrating this type of model into the finite element simulation, should allow the prediction of glass absorption and damage for nanosecond pulses.

In the ultrashort time regime, the film removal process was considered to a non-thermal ultrafast mechanism. In order to get a more in-depth understanding of this non-thermal mechanism, it would be of interest to carry out a study on the real time emission of electrons and ions during laser irradiation. Using this technique, the density of electrons
and ions can be examined as function of position over the sample, but also more importantly as a function of time. By detecting the emission of fast and slow electrons and ions as a function of applied fluence, further information on the film removal process may be identified.
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