<table>
<thead>
<tr>
<th>Title</th>
<th>Wavelength dependence of femtosecond laser ablation of thin gold films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Hastrup, Natalie</td>
</tr>
<tr>
<td>Publication Date</td>
<td>2014-05-26</td>
</tr>
<tr>
<td>Item record</td>
<td><a href="http://hdl.handle.net/10379/4414">http://hdl.handle.net/10379/4414</a></td>
</tr>
</tbody>
</table>

Some rights reserved. For more information, please see the item record link above.
Wavelength Dependence of Femtosecond Laser Ablation of Thin Gold Films

By Natalie Hastrup, M.Sc.

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 M. O’Connor
# Table of Contents

**Chapter 1 Introduction**
- 1.1 Objectives 3
- 1.2 State of the Art 6
- 1.3 Synopsis 8
- 1.4 Publications 9

**Chapter 2 Theory and Literature Review**
- 2.1 Ultra-short Laser Pulse Generation 12
  - 2.1.1 Femtosecond Laser Pulse Generation 12
  - 2.1.2 Chirped Pulse Amplification 13
  - 2.1.3 Pulse Picking 15
  - 2.1.4 Harmonic Generation 16
- 2.2 Thin Films 18
  - 2.2.1 Thin Film Deposition Technologies 18
  - 2.2.2 Thin Film Grain Microstructure 19
  - 2.2.3 Thin Film Properties 22
- 2.3 Interactions of Laser Light with Thin Films 24
  - 2.3.1 Laser Light-Thin Film Interaction 24
  - 2.3.2 Optical Properties of a Metal 26
  - 2.3.3 Electronic Heating 29
  - 2.3.4 Lattice Heating 30
  - 2.3.5 Computational Modelling 32
- 2.4 Laser Ablation Mechanisms 34
  - 2.4.1 Photophysical Ablation Mechanisms 35
  - 2.4.2 Photomechanical Ablation Mechanisms 38
- 2.5 Plasma and Plume Generation 40
  - 2.5.1 Electron Emission 41
  - 2.5.2 Atomic and Ionic Mass Emission 43
  - 2.5.3 Plasma Expansion 44
  - 2.5.4 Langmuir Probes 47
- 2.6 Nanoparticle Generation 51
  - 2.6.1 Nanoparticle Formation 51
  - 2.6.2 Factors affecting the Generation of Nanoparticles 53
  - 2.6.3 Techniques for Monitoring Material Ejection 56
  - 2.6.4. Schlieren Imaging 58
- 2.7 Section Summary 60

**Chapter 3 Equipment and Methods**
- 3.1 Thin Film Fabrication 61
  - 3.1.1 Set I Au Films 62
  - 3.1.2 Set II Au Films 64
- 3.2 Physical Properties of Thin Films 66
  - 3.2.1 Atomic Force Microscopy 66
  - 3.2.2 Film Thickness 67
  - 3.2.3 Grain Microstructure 68
  - 3.2.4 Film Roughness 70
  - 3.2.5 Film Adhesion 70
- 3.3 Optical Properties of Thin Films 71
3.3.1 Integrating Sphere 72
3.3.2 Reflectance Measurements 74
3.3.3 Transmittance Calculations 76

3.4 Femtosecond Laser System 77
3.4.1 Laser Electrical Signals 77
3.4.2 Laser Triggering and Timing 79
3.4.3 Standard Laser Parameters 81
3.4.4 Laser Ablation 84

3.5 Plasma Generation 86
3.5.1 Plasma Detection Setup 86
3.5.2 Signal Interpretation 90

3.6 Nanoparticle Generation 92
3.6.1 Nanoparticle Collection 92
3.6.2 Scanning Electron Microscopy 94
3.6.3 Nanoparticle Characterisation 96

3.7 Real-Time Visualisation 97
3.7.1 Schlieren Imaging Setup 97
3.7.2 Temporal Alignment 100
3.7.3 Spatial Alignment 101

3.8 Summary 102

Chapter 4 Thin Gold Film Characterisation 103

4.1 Introduction 103

4.2 Factors Affecting Grain Microstructure 106
4.2.1 Substrate 106
4.2.2 Surface Roughness 109
4.2.3 Film Thickness 112
4.2.4 Deposition Temperature 113
4.2.5 Deposition Rate 115

4.3 Factors Affecting Optical Properties 116
4.3.1 Data Collection 116
4.3.2 Film Thickness 117
4.3.3 Substrates 118
4.3.4 Laser Wavelength 122
4.3.5 Grain Microstructure 123

4.4 Factors Affecting Laser Ablation Threshold 124
4.4.1 Film Thickness 124
4.4.2 Substrate 126
4.4.3 Fabrication Method 127
4.4.4 Laser Wavelength 128
4.4.5 Grain Microstructure 129

4.5 Laser Ablation Threshold Summary 130
4.6 Conclusions 133

Chapter 5 Grain – Nanoparticle Size Relationship 135

5.1 Introduction 135
5.2 Laser Ablation 137
5.2.1 Laser Fluence for Nanoparticle Generation 137
5.2.2 Crater Profiles 139

5.3 Nanoparticle Generation 140
5.3.1 Influence of the Substrate 141
5.3.2 Influence of Grain Diameter 142
5.3.3 Influence of Film Thickness 144

5.4 Grain – Nanoparticle Relationship 146
Declaration

The work in this thesis is based on the research carried out at the National Centre for Laser Ablation (NCLA), School of Physics, National University of Ireland Galway. I, Natalie Hastrup, 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.
Acknowledgements

I will begin by thanking Gerard O’Connor for guiding and challenging me throughout this process, but also allowing me the freedom to forge my own path. I have enjoyed our discussions and am very appreciative of all the time you have dedicated to helping me. I would also like to thank Alan Conneely, Rebecca Nolan, Cormac O’Brien and Claire Bennett for their invaluable support and expertise. Thanks also to Mark Lang for supporting and encouraging me.

This research would not have been possible without the Irish Research Council EMBARK initiative funding and the Irish and European programmes that facilitated the fabrication of all the Au films. In particular, I would like to acknowledge Jaap Verheggen and the team at Tyndall, UCC and Eric van de Heuvel at Phillips, Eindhoven. Thanks also to the team at the Advanced Microscopy Lab at CRANN, TCD, for the access to equipment, training and expertise. I would also like to acknowledge the technical assistance of PJ Walsh and Conor McBrierty for the ion probe setup.

A special thanks to all of the people who have ensured that my caffeine levels were maintained and who helped me to retain some level of sanity throughout this PhD, in particular, James, Clare, Cormac and Leah. Thanks as well to everyone in the NCLA and the School of Physics for their moral support. I would also like to thank all of my friends and family who have encouraged and supported me from a distance; in particular Dan, Emma and Roger.

Finally, to the most important person in my life, thank you.
Abstract

The demand for efficient laser processing of materials is as strong as ever and this requires a deep understanding of the fundamental laser-material interactions. There has been a recent upsurge in the number of studies into the evolution of nanoparticles produced during laser ablation, originally to improve debris management, but more recently to utilise these nanoparticles in various applications. This study explores methods to improve the control of the nanoparticles produced and in turn gleans insight into the wavelength dependence of laser ablation mechanisms of thin gold (Au) films.

This experimental study has identified a fundamental difference in the interaction of a femtosecond laser pulse with thin Au films depending on the laser wavelength. A matrix of deposition rates, temperatures and substrates were used to generate a set of Au films (10-90 nm thickness) with a range of grain microstructures that were characterised using Atomic Force Microscopy (AFM). By accounting for the optical properties of the films, it was possible to examine the laser ablation mechanisms at three laser wavelengths, using the same absorbed fluence. A femtosecond laser (500 fs) was used to ablate each thin film at three laser wavelengths; 343 nm (UV), 515 nm (Green) and 1030 nm (IR). The ablation mechanisms at each wavelength were explored by monitoring the ejection of electrons, ions and nanoparticles from the film using a selection of equipment including a Langmuir probe, Scanning Electron Microscopy (SEM) and schlieren imaging.

The first key result was that laser ablation at UV and Green wavelengths resulted in the same linear relationship between the volume of the grain and the volume of the nanoparticles. Significantly, no relationship at all was observed when the film was ablated at the IR wavelength. This wavelength dependence was explained using the complementary computational study carried out by Lin and Zhigilei who identified the significance of non-equilibrium dynamics on the response of noble metals to laser pulses. Photons with $h\nu > 1.9$ eV exceed the interband transition threshold (ITT) of Au for the excitation of $5d^{10}$ electrons to
the Fermi level. According to Fermi’s Golden rule, the higher density of states associated with the d-band electrons compared to the s-band results in a greater absorption strength and heat capacity. Therefore if the ITT is exceeded, higher electron temperatures are reached, resulting in a substantial decrease in the electron-phonon coupling time. The electron-phonon coupling occurs on shorter time-scales than the mechanical relaxation of the material and thermoelastic ablation of the Au film ensues. In this study, the three laser wavelengths of UV, Green and IR had photon energies of 3.62 eV, 2.41 eV and 1.21 eV, respectively. Therefore laser absorption of either UV or Green pulses exceeded the ITT and lead to thermoelastic ablation of the film into the grains. Since the ITT was not achieved with IR photons, ablation proceeded over a longer timescale, whereby melting of the film occurred and any relationship between the grains and nanoparticles was effectively lost.

This fundamental material response of Au to femtosecond laser pulses of different laser wavelengths was also demonstrated in the electronic emission, which was measured using a Langmuir probe under vacuum conditions. A substantially higher number of emitted electrons were detected following UV or Green laser pulses compared to IR, as well as the notable addition of thermionic emitted electrons. The number of detected charges was then used to calculate the contribution of Rayleigh-charge instabilities to the break up of grains into smaller nanoparticles at the UV and Green wavelengths. Finally, the development of a schlieren imaging setup facilitated the real-time visualisation of the expansion of the nanoparticle plume at each wavelength and once again demonstrated the significance of the photon energy on the laser ablation mechanism and nanoparticle generation.
Chapter 1
Introduction

The continued prominence of laser processes in everyday and industrial applications highlights the importance of probing the science behind them. The study of such processes on a fundamental level ultimately leads to the invention or improvement of products that are safer, cheaper and more effective. The ongoing pursuit of ever smaller technological devices has resulted in the use of sub-micron thick films, as opposed to the bulk equivalent. The quantum confinement effects that exist for such thin films (< 100 nm) result in unique physical properties that are then exploited in their application [1]. These applications require precision laser processing and there is consequently a drive to understand and control the interaction between the laser and thin films. The laser processing of thin films compared to bulk materials is complex, primarily due to their variable properties, but also due to the contribution of the substrate, onto which the film is deposited. Therefore laser processing of thin films cannot simply depend on the plethora of available data on the laser processing of bulk materials.

The thin films selected for this study are Gold (Au), which are used in many applications in optical components and electronic devices, owing to their chemical inertness and stability. Applications for laser processed thin Au films include electromechanical systems, sensors, electronic textiles or bioengineering [2]. Typically, Au thin films are grown on inert insulator substrates, but there is also an interest in investigating thin Au films on Silicon substrates with a view to integrating biosensors on already established Silicon wafers used in electronics [3]. The substrates considered in this study were Sapphire, single crystalline
Quartz and Silicon. To achieve precision laser processing of thin films, the contribution of the laser parameters and material properties to the final product must be understood. This study investigates the interaction of a femtosecond laser pulse with a range of Au films of different microstructures and thicknesses by monitoring the ejected matter during laser ablation.

The laser-material interaction can be explored by monitoring the plasma components ejected from the material during laser ablation. If sufficient energy is absorbed by the material, electrons and ions are ejected and propagate away from the surface. These electrons and ions can be detected within a vacuum setup to deliver valuable information on their number densities and their temporal and spatial evolution [4, 5]. The profile of the ejected components can deliver insight into the interaction of the laser with the electronic system of the target and the subsequent mechanisms of ablation.

During laser processing, debris is generated in the form of nanoparticles, which has prompted numerous studies into their formation and evolution. There are four primary reasons for the interest in these laser-generated nanoparticles; Firstly, nanoparticles are a by-product of laser ablation and it is therefore practical to contemplate uses for the debris generated. Secondly, the debris that re-deposits into the ablated areas can jeopardise the quality of the laser processed product. Thirdly, the formation of nanoparticles during laser ablation poses a hazard that is not yet fully characterized due to the lack of data detailing the size and movement of these nanoparticles following ablation. A greater analysis of this debris is required after which it can be matched to the ongoing toxicology studies in the medical sector [6]. Finally, through investigating nanoparticle generation during laser ablation, a valuable insight may be gained into the laser ablation mechanisms in thin films. A greater knowledge of ablation mechanisms and debris removal facilitates many thin film applications that require the meticulous removal of material and precise nanostructuring of thin films.

Laser generated nanoparticles can be collected by ablating the target material submerged in a liquid [7] or by supporting the nanoparticles on a substrate, as is the case in this study. Gold nanoparticles are of particular interest, because of their inertness and interesting optical properties, but also because of their
potential biomedical applications in nanosurgery, bio-sensing [8], precision drug delivery, catalysis [9], and cancer detection and therapy [10, 11]. The laser generation of nanoparticles offers the important advantage over chemically synthesised nanoparticles, that additional chemicals, solvents and surfactants are optional.

1.1 Objectives

The overall objective of this study is to examine the femtosecond laser ablation of thin Au films to identify the role of material properties; such as grain microstructure, and laser properties; such as wavelength. This study will monitor the ejection of the plasma and nanoparticles from a range of thin Au films during laser ablation to gain information about the ablation mechanisms. With a deeper understanding of material ejection processes, the control of nanoparticle generation may be improved. The study aims to provide answers to the following two key questions:

1) What impact does the grain microstructure of thin films have on femtosecond laser ablation of thin Au films and nanoparticle generation?
2) What impact does the photon energy have on femtosecond laser ablation of thin Au films and nanoparticle generation?

The objectives of the study are broken down into three sections that correlate with the Results Chapters 4, 5 and 6, respectively.

1) Thin Film Characterisation

The overall objective of Chapter 4 was to characterise the Au films and lay the groundwork for the more probing studies presented in the following results chapters. It was imperative to build up knowledge of the grain microstructure,
optical properties and laser ablation threshold fluences of the different Au films for the interpretation of later results. The key objectives of this chapter are:

- To ascertain how the grain microstructure of thin Au films can be controlled by comparing films of different thicknesses, substrates and fabrication conditions.

- To identify a method to determine the amount of incident light that is absorbed by a thin Au film and establish the physical properties that affect the optical properties.

- To explore the consequences of discussing laser ablation of films in terms of the, commonly used, applied laser fluence and ascertain whether the incorporation of the films optical properties to give the fluence absorbed by the material is a more suitable parameter.

- To determine the key physical properties of Au films that impact their absorbed ablation threshold fluence.

2) Grain – Nanoparticle Relationship

The overall objective of Chapter 5 was to explore the impact of the grain microstructure of thin films and the laser wavelength on the laser generation of nanoparticles. The purpose of this Chapter was to supplement the understanding of the processes of laser ablation and nanoparticle generation with a view to gaining more control over their production and size.

- To establish a method to compare the laser generation of nanoparticles at different laser wavelengths, whereby the absorbed laser fluence is the same for all Au films.

- To identify the role of both the film thickness and the grain diameter on the size of Au nanoparticles generated during femtosecond laser ablation.
• To explore whether a relationship exists between the size of the Au grain microstructure and the size of the nanoparticles that are generated during femtosecond laser ablation.

• To determine whether the grain microstructure and laser wavelength are significant in the mechanism for femtosecond laser ablation of thin Au films and nanoparticle generation.

3) Wavelength Dependence of Material Ejection

The overall objective of Chapter 6 was to further probe the wavelength dependence of laser ablation by monitoring the electron, ion and nanoparticle ejection from the films during ablation. Two setups are required including a Langmuir probe setup and a schlieren imaging setup to understand the dynamics of the ablation processes at different wavelengths.

• To develop a Langmuir probe setup under vacuum conditions to probe electron and ion emission from Au films during laser ablation.

• To determine whether there is a wavelength dependence of the emission of electrons from 20 nm thick Au films following the absorption of the same laser fluences.

• To determine whether there is a wavelength dependence of the emission of ions from 20 nm thick Au films following the absorption of the same laser fluences.

• To ascertain whether the emission of electrons from the Au films could result in Coulombic repulsion between the remaining positively charged ions and thus contribute to the ablation mechanism or the subsequent break up of the grains.

• To develop a schlieren imaging setup to image the generation of nanoparticles and establish any differences at different laser wavelengths.
1.2 State of the Art

The impact of fundamental studies, such as this one, can resonate with a variety of academic and industrial research groups. Two areas which could potentially benefit from the findings in this study are in the optimisation of thin film laser processing and in the laser generation of nanoparticles. The current state of the art for both these areas are discussed in this section.

Thin Film Laser Processing

In industry, the typical approach to laser processing of a new material is to identify a process window of particular laser parameters, for which the desired laser processing is achieved. This is a time-consuming process that not only involves trying all lasers and parameters and then analysing each set of data, but if the optimal laser or parameters are not achievable with the lasers possessed, the ideal setup may be overlooked. To overcome this complex and lengthy process, fundamental studies that deliver a greater understanding of the laser-material interaction and the ablation mechanisms occurring would streamline this process. This knowledge would empower studies to undergo a much smaller matrix of laser parameters, before identifying the process window for the material. This fundamental study will investigate the impact of the laser wavelength on the absorption and ablation mechanisms of thin Au films. The study will explore the impact of the parameters used for thin film fabrication on the laser ablation process, in particular the grain microstructure of the thin films. Finally, this study will accumulate information about the ejected debris during laser ablation, which may provide insight into the laser ablation mechanisms occurring at different fluences and wavelengths.
Nanoparticle Generation

The state of the art in nanoparticle generation is chemical synthesis, though laser generation of nanoparticles is becoming increasingly competitive, as it is lower cost, simple, fast and environmentally friendlier (as additional chemicals are not required), as well as offering an unlimited range of materials [7, 12, 13]. Furthermore, the process offers unique control of the nanoparticle surface, charge and the collection medium. The current limitation of this process is the control of the nanoparticle size compared to chemical production that can produce monodisperse nanoparticles with standardly less than a 10% variation in size. The chemical synthesis method is principally limited by the inclusion of chemical precursors that may not be suitable in all applications. The chemical precursors are typically toxic in the body, thereby ruling out biomedical applications. Therefore if it is possible to further optimise the laser generation of nanoparticles, the process would prove advantageous in a multitude of applications, such as for drug delivery or biosensors. These are the applications where the laser generation of nanoparticles could offer a substantial advantage, whereby the synthesis method produces nanoparticles in a liquid that have high colloidal stability and excellent conjugation compatibility with biomolecules. The addition of ligands or chemicals to the synthesis method is therefore a choice not a necessity.

Many studies have contributed to the assimilation of data and the drive to optimise the conditions for producing laser generated nanoparticles with controlled diameters and small dispersions. Studies have investigated the influence of different laser properties [14, 15], different material properties [7, 11] and ablation in different environments [16-18]. Most studies favour the generation of nanoparticles in a liquid ambient, to simplify their collection and to better control their size distribution [7, 16, 19]. The method typically entails the ablation of a bulk material immersed in a liquid, with the application of multiple laser pulses, over a period of a few hours. The generated nanoparticles interact with multiple pulses and fragment until a uniform size of nanoparticles are generated. This study will supplement this data, with information about the significance of laser wavelength and the grain microstructure on nanoparticle generation.
1.3 Synopsis

This thesis contains seven chapters including this Introduction chapter. The synopsis of the remaining chapters is as follows:

**Chapter 2** provides the background theory to the techniques, analysis and data interpretation involved in this thesis. The chapter also reviews the relevant literature in this area of research and identifies where the gaps in knowledge are.

**Chapter 3** presents the fabrication process for the Au thin films and details the equipment and techniques used to characterise them. The various femtosecond laser setups are described and discussed. Finally, the experimental methods for nanoparticle and plasma generation are presented along with the data analysis techniques.

**Chapter 4** is the first Results chapter, which presents the characterisation of the different Au films; such as grain microstructure, optical properties and ablation threshold fluences. The optical properties of each film are combined with the incident laser fluence to establish the fluence absorbed by the films.

**Chapter 5** explores the relationship between the grain microstructure of Au films with the nanoparticles generated during femtosecond laser ablation. The wavelength dependency of this relationship is also determined by establishing a method, whereby the absorbed fluences at each wavelength are comparable.

**Chapter 6** builds on the outcomes in Chapter 5 by investigating the wavelength dependency of the plasma generation during laser ablation by using a Langmuir probe in a vacuum chamber. Finally, the evolution of the nanoparticle plume generated during laser ablation at different laser wavelengths was imaged using a schlieren imaging setup.

**Chapter 7** summarises the key findings of the thesis and also suggests ideas for building on this thesis in terms of future work.

**Appendices** provide a list of acronyms, abbreviations and symbols used, as a guide to the reader. Information is also included about the author’s publications and communications throughout the duration of this study.
1.4 Publications


Chapter 2
Theory and Literature Review

This chapter provides the background theory required for the interpretation of the results presented in later chapters and also investigates the position of this study with respect to the current literature available. The chapter begins with Section 2.1 describing the process of producing ultra-short laser pulses and harmonic generation. These laser pulses are used to laser ablate thin Au films with different film thicknesses and grain microstructures. The mechanisms for thin film fabrication and the factors impacting the film properties are then presented in Section 2.2. The interaction of ultra-short laser pulses with thin films is then discussed in Section 2.3, in terms of the variable optical properties of thin films and also the heating of the electronic and lattice sub-systems. The complexities of defining laser-material interactions with a thin film, compared to bulk materials, are also highlighted. Laser ablation mechanisms are then explored in Section 2.4, with particular focus on the mechanisms discussed in the literature for metals. Sections 2.5 and 2.6 discuss the ejection of material during laser ablation, with respect to the generation of plasma, plume and nanoparticles. Section 2.7 then summarises the literature review and identifies the gaps that this study aims to fill.
2.1 Ultra-short Laser Pulse Generation

Progressing from nanosecond laser pulses to ultra-short pulse generation has enabled rapid deposition of laser energy into a material. This facilitates precise material processing with minimal residual damage (defined by the heat affected zone). Additionally, ultra-short laser pulses deliver the energy prior to the ejection of material and therefore do not encounter the complex interactions of the laser with the plume, as experienced with nanosecond pulses.

The theory of ultra-short laser pulse generation, amplification and harmonic generation will be discussed in terms of the femtosecond laser system (Amplitude S-Pulse) used throughout this study. The system comprised of a laser head for pulsed laser generation and a bespoke optical interface box for harmonic generation and power attenuation.

2.1.1 Femtosecond Laser Pulse Generation

The laser head comprises of the oscillator, optics for pulse stretching and compression, amplifier and acousto- and electro-optic modulators. Figure 1 provides a schematic diagram of the laser-head and the laser pathway for pulsed femtosecond laser generation.

The oscillator comprises of a Fabry-Pérot cavity with two mirrors at either end and a Ytterbium Vanadate crystal in-between. Ytterbium doped crystals offer advantages over Titanium:Sapphire lasers, such as they can be directly diode-pumped, they have high thermal efficiency and can generate femtosecond laser pulses with high average power.

The crystal is pumped using a diode laser to excite electrons to a higher energy state and force a population inversion. As the electrons return to the ground state, photons are released in all directions. Only the photons travelling in the direction normal to the end mirrors are reflected between the mirrors. These photons pass
through the crystal and result in more photons being emitted. The constructive and destructive interference between the different waves results in standing waves or modes in the cavity. The standing waves relate to the only frequency of light that will continue to oscillate within the cavity. When the different oscillating modes are in a fixed phase relative to one another, the oscillator is said to be mode-locked. The greater the frequency separation between these modes, the shorter the achievable pulse duration. When mode-locking is achieved, the different oscillating modes constructively interfere with one another and result in a laser pulse with temporally, energetically and spatially matched photons. The oscillator results in a weakly powered (< 20 nJ), 250 femtosecond, 1030 nm laser pulses at a repetition rate of 30 MHz.

Figure 1: Schematic diagram illustrating the laser beam path within the laser head containing the femtosecond Oscillator, the Pulse Stretcher, Pockel cell and Amplifier and Pulse Picker and finally the Pulse Compressor. The beam path is associated with the fundamental wavelength (1030 nm).

2.1.2 Chirped Pulse Amplification

The amplification of ultra-short laser pulses is more complex than for longer pulse durations, since the laser intensities achieved would result in damage to the optics and the gain medium. Chirped Pulse Amplification (CPA) was developed by Mourou and Strickland to overcome this problem [20]. CPA uses a pair of
diffraction gratings either side of a set of lenses, to temporally and spectrally stretch the oscillator laser pulse, thereby reducing its energy. A diagram of the CPA system has been produced in Figure 2. The first set of gratings (1) shown in Figure 2 cause the positive dispersion of the laser beam, in which light with a lower frequency will take a shorter time to travel through the gratings than higher frequencies. This results in the temporal and spectral dispersion of the laser pulse.

Once the laser pulse has been temporally and spectrally stretched, it passes through the Pockel cell and then the Amplifier. The mode-locked oscillator seed laser operates at very high repetition rates (MHz) and therefore a Pockel cell is used to reduce the repetition rate of the laser pulses and consequently increase the pulse power. The Pockel cell is positioned just before the Amplifier as shown in Figure 2. The Pockel cell is an electro-optic device that comprises of voltage-controlled wave plates that can be orientated to either prevent or allow the laser light through based on the polarization of light. The Pockel cell initially prevents

**Figure 2**: Pictorial description of the Chirped Pulse Amplification (CPA) process. A weak oscillator pulse passes through a pair of diffraction gratings, which temporally and spectrally stretch the pulse (1). The stretched low power pulse passes through the Pockel cell before it is amplified in the regenerative amplifier to give a higher energy pulse (2). The amplified stretched pulse is then recompressed using a second set of gratings (3). Finally a high energy ultra-short pulse is produced (4).
optical amplification by directing light with a certain polarization out of the cavity. If the Pockel cell allows the light into the amplification cavity, the energy stored reaches a maximum and is called gain saturated. This orientation is denoted as having a low Q-factor. The Pockel cell is then switched to allow another pulse into the amplifier cavity and an ultra-short pulse is released. This orientation is denoted as having a high Q-factor. A fast transition between high and low Q-factors results in the production of laser pulses.

The regenerative amplifier acts to amplify the stretched laser pulses and gives rise to high intensity laser pulses. The amplifier comprises of another cavity with a Ytterbium doped medium. The medium is pumped with a diode laser to achieve maximum gain, before a single femtosecond pulse enters the cavity. The laser pulse is reflected within the cavity and amplified, before a single high energy laser pulse is released.

Once the pulse has passed through the Pockel Cell and Amplifier, the laser pulse is then re-compressed. The method for re-compression of the pulse is simply the reverse of pulse stretching described earlier and uses a second set of diffraction gratings (3), shown, in Figure 2. This second pair of grating causes negative dispersion of the laser pulse, whereby the pathlength for light with higher frequencies is shorter than for the light with lower frequencies. The combination of the stretcher followed by the compressor gratings act to cancel out the dispersions induced and results in a temporally and spectrally uniform laser pulse once more.

2.1.3 Pulse Picking

These amplified pulses then pass into the Pulse Picker (PP). The PP operates using an acousto-optic modulator (AOM) switch to pick pulses, thereby giving a lower repetition rate of pulses, but with the same energy. An acousto-optic modulator functions when an oscillating electric signal causes a transducer to vibrate, which creates sound waves in the glass. These sound waves in the glass are periodic planes of expansion and compression that alter the refractive index
in the glass. The incoming light scatters off this periodic modulation and interference occurs. The light passing through the glass experiences Bragg diffraction due to the periodic changes in refractive index and therefore the beam polarization is altered. The light has a slightly altered frequency and/or direction, which is controlled by the frequency of the sound wave. The pulses with the required direction and frequency can pass through an aperture, whereas the other pulses are blocked. The speed of the AOM is determined by the temporal distance of pulses in the pulse train (i.e. repetition rate). AOMs are typically favoured over EOMs as they require much lower voltages and therefore have lower power consumption. The purpose of the PP in this system is to improve pulse-to-pulse stability when varying the repetition rate.

2.1.4 Harmonic Generation

From the laser head, the ultra-short, amplified, picked laser pulses exit out of the main output hole and enter into the bespoke interface box. The fundamental 1030 nm (IR) laser beam is horizontally polarized and on entering the interface box is rotated to be vertically polarized. The vertically polarized IR beam then passes through a tunable wave plate and onto a polarized mirror. The tunable waveplate is controlled by an auto-correlator and alters the polarization of the beam. The polarized mirror on the other side of the motorized wave plate is transparent to vertically polarized light, but reflects horizontally polarized light. The auto-correlator can therefore be adjusted to select whether the amplified beam is directed to the IR output or directed to the harmonic crystals as illustrated in Figure 3. The auto-correlator can also be used to adjust the laser power at the interface box outputs by selecting the beam path.
Figure 3: Schematic diagram of the bespoke optical interface box, in which different laser beam paths are possible, for the harmonic generation of three different laser wavelengths. The fundamental wavelength, 1030 nm, can exit the interface box or pass through a second Harmonic Crystal and third Harmonic crystal for the generation of laser wavelengths 515 nm and 343 nm. The polarisation of each laser pathway is indicated.

When the beam is horizontally orientated, it is reflected to pass through the harmonic crystals. The interface box contains a second order harmonic generation (SHG) lithium triborate (LBO) crystal, followed by a third order harmonic generation (THG) barium borate (BBO) crystal in the beam path. The wavelength of the fundamental laser is 1030 nm (IR), and 515 nm (Green) and 343 nm (UV) wavelengths are achieved through non-linearities of the crystals. Frequency doubling in the SHG occurs when two IR photons passing into the SHG crystal and results in the generation of one Green photon. Further non-linear frequency mixing can then occur in the THG crystal as both Green and IR photons will pass through the crystal and a photon of each wavelength can combine to result in a single UV photon. The crystals used are optimized to be the appropriate length to result in optimal phase matching between combining photons. This is important to maximize power output at these wavelengths. The Green waves that are created at the start of the crystal will differ in phase to those produced at the end of the crystal. This is because the IR and Green waves have different velocities in the crystal, owing to the different refractive indices for the different wavelengths.

The polarisation of the Green laser beam is horizontally orientated on exit, whereas the UV laser beam is vertically orientated. The mirrors that follow the
harmonic crystals are dichroic, which filter out other wavelengths and direct the beam paths to different outputs of the interface box.

2.2 Thin Films

Thin films of Gold, Au, were the target material chosen for this study of laser-material interactions and laser ablation. The grain microstructure of the films was identified as a potential avenue of interest, in terms of the laser-material interaction. The possibility of controlling the grain microstructure to acquire a range of grain sizes demanded an exploration of the various deposition methods and parameters available and to understand the deposition mechanisms for thin metal films.

2.2.1 Thin Film Deposition Technologies

High precision, thin film (< 100 nm) fabrication is now achievable via a range of competing methods, each with its own specifications and limitations. A method is typically selected based on the requirements for material, film thickness, contaminants, deposition rate and temperature, grain microstructure, cost and so on. Thin film fabrication methods include physical vapor deposition (PVD) e.g. sputtering, e-beam evaporation and pulsed laser deposition or chemical vapor deposition (CVD) e.g. plasma enhanced CVD or low pressure CVD.

E-beam evaporation and sputtering were selected to fabricate the films for this study based on material, control of grain microstructure, availability and cost. Previous studies in the group had fabricated metal films via e-beam evaporation that had offered a suitable range of grain microstructures required for this study. Sputtering was also selected as it offered potentially greater control of the grain microstructure with variable deposition rates and temperatures. A summary of the features of the two deposition techniques is displayed in Table 1.
Table 1: Summary of thin film deposition technologies: E-beam evaporation and Sputtering [21].

<table>
<thead>
<tr>
<th></th>
<th>E-Beam Evaporation</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. Deposition Rate</td>
<td>10 - 100 Å / s</td>
<td>100 Å / s</td>
</tr>
<tr>
<td>Impurities</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Thickness Control</td>
<td>Poor</td>
<td>Controllable</td>
</tr>
<tr>
<td>Film Density</td>
<td>Average</td>
<td>Good</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Poor</td>
<td>Excellent</td>
</tr>
<tr>
<td>Grain Size</td>
<td>Poor Control</td>
<td>Controllable</td>
</tr>
<tr>
<td>Cost</td>
<td>Average</td>
<td>Average</td>
</tr>
<tr>
<td>Surface Damage</td>
<td>Very Low</td>
<td>Ionic Bombardment</td>
</tr>
</tbody>
</table>

These deposition technologies and the parameters used for thin Au film fabrication are discussed in Chapter 3.1. The following section describes the formation of grains in thin films.

2.2.2 Thin Film Grain Microstructure

Metal films are polycrystalline materials and therefore comprise of a number of crystallites or grains, which are separated by grain boundaries. The grain microstructure describes the localised areas within the film where the crystal orientation is aligned in a particular orientation. Grain boundaries are the interfaces, at which crystals of differing orientations impinge during film fabrication. Grains can range in size, from nanometers up to millimeters and are influenced by the fabrication method and conditions, the interaction of the film atoms with the substrate and the film and substrate properties e.g. film thickness, grain size, surface roughness, impurity content, defect density [22, 23].

For both e-beam evaporation and sputtering, the depositing atoms impinge on a substrate surface, whilst in molten form. The strength of the interaction between the depositing atoms with the substrate has an important bearing on the microstructure of the film that forms [24]. The Young’s equation (Equation 1) describes the tendency of the liquid to ‘wet’ the substrate surface and affects the
growth mechanism that ensues [25]. The equation determines the contact angle, \( \theta_c \), at the three interfaces between the substrate (S), the liquid depositing atoms (L) and the air (G). These interfaces are described using the surface free energy, \( \gamma \), at each interface.

\[
\cos \theta_c = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad \text{Equation 1}
\]

The contact angle is therefore an indication of the interaction strength between the depositing droplets and the substrate, as illustrated in Figure 4.

![Figure 4](image)

*Figure 4*: Illustration of the surface energies relating to the different interfaces govern the contact angle between depositing liquid droplets and a solid substrate surface. (a) represents a poor wetting on the surface with a contact angle > 90\(^\circ\) and (b) represents a strong wetting of the surface by a contact angle < 90\(^\circ\).

When the contact angle is high (\( \theta_c > 90^\circ \)) there is a weak interaction between the liquid and substrate and the droplet remains almost spherical on the surface, as shown in Figure 4a. When the contact angle is low (\( \theta_c < 90^\circ \)) the liquid interacts strongly with the substrate and therefore spreads out on the substrate surface, as shown in Figure 4b. The balance of attractive and cohesive forces between the film atoms and the substrate governs the tendency towards one of the three main growth mechanisms for thin films; island growth (Volmer-Weber), Layer-by-layer (Frank van der Merde) or a combination (Stranski-Krastinov).

If the interaction between the film atoms is greater than for the substrate (i.e. \( \theta_c > 90^\circ \)), then Volmer-Weber (or island) growth is observed. However, if the interaction between the substrate and film atoms is greater than the interaction between the film atoms (\( \theta_c < 90^\circ \)), Layer-by-Layer growth is typical. The final mechanism, Stranski-Krastinov, is a combination of the two previous mechanisms, in which initially one or two monolayers will form, followed by
island growth. Materials, such as metals, form strong chemical bonds between the atoms and if the surface energy of the Au film, $\gamma_{LG}$, is greater than the surface energy of the substrate, $\gamma_{SG}$, then Volmer-Weber growth ensues. The surface energy of noble metals is typically in the range 1-2 J m$^{-2}$ and would be classed as an intermediate surface energy. For insulators, such as the substrates used in this study, the values for surface energy are approximately 0.3-1 J m$^{-2}$ and these are considered in the low range. Therefore Au has a higher surface energy than the substrate and therefore do not easily wet the low surface energy substrates and thus Volmer-Weber is the energetically favoured growth mechanism.

The Volmer-Weber growth mechanism begins with nucleation, followed by growth and coalescence. The deposition of metal atoms on the substrate builds up in a highly localized way until this cluster of atoms reaches a critical radius and forms thermodynamically stable nuclei. These nuclei begin to grow via condensational growth, during which, atoms are deposited on the surface of the nuclei. From these nuclei, coalescence can occur in which two nuclei have grown so large that they impinge on one another [24]. This impingement can proceed in one of two ways depending on the phase of the nuclei; if in solid form, the grain boundaries appear between two islands or if in liquid phase, the islands coagulate and form larger grains [26].

The substrate can also contribute to the films microstructure in terms of lattice mismatch, which induces strain on the film, and also in terms of the crystal orientation of the metal film that predominantly grows. For example, Au will characteristically form face-centered cubic (fcc) structure in real space, but could be strained into the same crystal orientation as the substrate, particularly in nanometer thick films [27, 28]. This has been shown for Au films were deposited onto substrates of glass, Mica and Silicon, where the Au coating orientated along the substrate crystal to differing degrees [25].

As the film grows thicker, the Au films become increasingly continuous, which also impacts the film density and grain microstructure. Smith et al. determined that Au films deposited by conventional evaporation only became continuous at thicknesses of 15 nm [29]. The grain microstructure that forms throughout the depth of the film is largely dependent on the deposition temperature relative to
the melting temperature of the material. Kaiser produced a comprehensive review of the film microstructures that form and categorised them into three zones [24]. Zone I relates to low depositing atom mobilities ($T_s / T_m < 0.3$), in which amorphous layers form with fine grains throughout the depth of the film and is often porous. Zone II relates to higher mobilities ($0.3 < T_s / T_m < 0.5$), in which nucleation and growth occurs freely until impingement, thus forming columns [30]. Zone III relates to the highest mobilities ($T_s / T_m > 0.5$), in which the rough grained structure forms.

2.2.3 Thin Film Properties

There is a noticeable issue in the literature that studies apply values determined for various properties of bulk materials to thin films, despite the vast differences that often exists. Fortunately, there is an increasing number of studies into the accurate measurement or calculation of properties of thin films. To illustrate this point, some key properties that differ for Au thin films compared to the bulk equivalent are given below.

**Lattice Parameter:** The lattice parameter of metal thin films is not a material constant, but depends on the layer thickness. Au films of 10 nm thickness had a lattice parameter of 4.084 Å, which fell approximately exponentially to 4.072 Å for 90 nm thick films, as measured with X-ray diffraction [2]. This was explained through stress relaxation during the growth of Au clusters.

**Optical properties:** The optical properties are also affected by the film thickness e.g. the transparency of Au films increases, as the film thickness decreases. The interface between the film and substrate therefore increasingly affects the observed optical properties. Imperfections such as surface roughness and grain boundaries can also increase scattering of incident light.

**Plasma frequency:** There is an increase in plasma frequency with film thicknesses of 3 nm up to 15 nm, of 3 eV (413 nm) and increasing to the bulk value for Au of 9.02 eV (137 nm) [2]. This increase in plasma frequency with
film thickness is explained through Mie theory, whereby a red-shift is observed with decreasing cluster size. The plasma frequency is closely related to the concentration of free carriers, which increases with cluster size.

**Electron-phonon coupling time:** The electron-phonon coupling time in heated Au films has been shown to be almost an order of magnitude lower than the bulk value [27]. This time is dependent on the carrier density and the penetration depth of the laser, which is typically limited to the film thickness.

**Resistivity:** There is typically a rapid decline in the resistivity of Au when the film thickness exceeds 5 nm, which relates to the transition between electrical discontinuity to electrical continuity [2]. The resistivity of thin Au films has been measured as an order of magnitude higher than that reported for bulk metallic Au (\(R = 2.5 \times 10^{-6} \ \Omega \ cm\)) [2]. This increase in resistivity is due to the size effect described by Matthiessen rule [31]. Matthiessen’s rule accounts for the reduction in electron mobility due to scattering sources in the material, such as impurities and lattice phonons.

**Thermal conductivity:** The thermal conductivity was measured by Yu et al. with a Micropulse Calorimeter and established that the thermal conductivity of copper thin films was typically one order of magnitude smaller than that of the bulk value [32]. The difference between the thermal conductivity of a thin film (< 100 nm) and the bulk material is usually attributed to surface boundary scattering and/or grain boundary scattering. The smaller the grains, the greater the number of grain boundaries in the material and these boundaries typically reduce the electrical and thermal conductivity of the material.

**Melting Temperature:** The melting point of bulk Au is 1336K, but this decreases as the size of the material reduces to the nanoscale [2]. This effect is known as melting point depression and is a consequence of increasing surface area-to-volume ratio as the film thickness decreases. This depression begins for films and particles below 20 nm in size for Au but becomes a dominant factor below 5 nm [33].
2.3 Interactions of Laser Light with Thin Films

This section details the interaction of laser energy with the thin films, firstly through the electronic system before coupling the energy to the lattice system.

The laser energy absorbed by a bulk material occurs over a depth characterized by the optical \((1/\alpha)\) penetration depth and the distribution of this thermal energy by the ballistic electron motion and the thermal penetration depth. However, for thin metal films, the energy deposited in the material is effectively confined by the film thickness \((z)\) and the laser beam diameter \((xy)\), assuming that the substrate is transparent to the laser wavelength and has a low thermal conductivity. The apparent simplicity of the confined heated volume in a thin film is countered by the complexities introduced by the addition of the film/substrate interface within the laser interaction depth. The optical and thermal properties of the substrate can therefore also contribute to the laser-thin film interaction. The system is also further complicated by the variation of material properties with film thickness. This section explores the considerations required for laser-thin film interactions.

2.3.1 Laser Light-Thin Film Interaction

The optical response of a material to incident laser light is governed by the electronic system. The three primary responses of a material to incident laser light at the Air / Film interface are reflection, transmission and absorption. The optical properties of a material define the percentage of the incident light that will be reflected, transmitted and absorbed. The optical properties of the film also vary with the laser properties, such as wavelength.

The optical interactions are further complicated in multi-layer systems, such as thin films, due to the presence of the substrate. This introduces an additional interface (Film / Substrate), at which any laser light that transmits through the film, can again be reflected, transmitted and absorbed. Figure 5 illustrates five of
the many interactions that can occur between the incident laser and a thin film stack.

Another factor to consider for the optical interaction of laser light with a thin film is the scattering phenomenon. Scattering occurs when the wavelength of laser light is equal or greater in size than the particles, with which it is interacting. As described in Section 2.2.2, the thin films are polycrystalline and the grain boundaries can give rise to scattering of the laser light. If the surface has a high roughness, scattering can also occur. The scattering events take place on time-scales of 100 fs in metals, therefore much quicker than the radiative lifetimes, which are on the nanosecond timescale [34].

**Figure 5**: Interactions of laser light with Au thin film system.

1. Laser light is reflected at Interface 1
2. Laser light is absorbed by Au
3. Laser light is transmitted by Au and either
   (a) reflected at Interface 2 and transmitted through Au or
   (b) reflected at Interface 2 and absorbed by Au
4. Laser light is transmitted through Au and through substrate
5. Laser light is transmitted through Au and absorbed by the substrate
2.3.2 Optical Properties of a Metal

Metals obey the laws of linear optics for ultra-short laser pulses up to intensities of $10^{15}$ W cm$^{-2}$ [35]. The absorption and refraction of incident light by a metal can be described using the complex refractive index, $\tilde{n}$.

$$\tilde{n} = n + ik$$

Equation 2

where $n$ and $k$ are the real and imaginary parts of the complex refractive index, respectively. The values of $n$ and $k$ are governed by the electronic system of the material and vary with incident laser wavelength. The imaginary part, $k$, is termed the extinction coefficient and describes the attenuation of an electromagnetic wave, due to absorption, as it propagates through the material. The Beer-Lambert law describes the attenuation of the incident laser intensity, $I$, as a function of distance propagated into the material, $z$.

$$I(z) = I_0 \exp(-\alpha z)$$

Equation 3

where $\alpha$ is the wavelength dependent linear absorption coefficient and $I_0$ refers to the incident laser intensity.

$$\alpha = \frac{4 \pi k}{\lambda}$$

Equation 4

The depth into the material, to which, the intensity of the laser beam falls to $1/e$ of the initial value, is termed the optical penetration depth and is $1/\alpha$. The depth over which the intensity of incident laser light, $I_0$, will be attenuated was calculated for Au using values in Palik [36] at the three laser wavelengths used in the study, 343 nm (UV), 515 nm (Green) and 1030 nm (IR) and is shown in Figure 6. The optical penetration depth at UV, Green and IR wavelengths is 14.85 nm, 19.39 nm and 11.59 nm, respectively.
The fraction of laser light that is not absorbed by the material is either transmitted or reflected. Equation 5 gives the coefficient of reflection, \( R \), at the interface between the air and the material, when the incident light is aligned with the normal to the material.

\[
R = \left| \frac{n-1}{n+1} \right|^2 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad \text{Equation 5}
\]

The reflectance of a film has also been shown to depend on the film thickness, \( h \) [37, 38]. Expressions were developed based on Fresnel equations of the reflection and transmission at the air/film interface and the film/substrate interface [38].

\[
R = \frac{r_1^2 + 2r_1r_2\cos2\delta + r_2^2}{1 + 2r_1r_2\cos2\delta + r_1^2r_2^2} \quad \text{Equation 6}
\]

\[
r_1 = \frac{n_1 - n_0}{n_1 + n_0} \quad r_2 = \frac{n_2 - n_1}{n_2 + n_1} \quad \text{Equation 7}
\]

\[
\delta = \frac{4\pi h}{\lambda} n_1 \quad \text{Equation 8}
\]

where \( n_0 \), \( n_1 \) and \( n_2 \) refer to the refractive indices of air, film and substrate, respectively. These equations account for potentially multiple incoherent reflections occurring at the interfaces and consequent variations in the reflection, transmission and absorption.
The exact optical response of a metal is dominated by the conduction band electrons, often referred to as free electrons. Reflectivity for metals is high relative to other materials, due to the high density of free carriers. The dielectric function, \( \varepsilon \), describes the propagation of an electromagnetic wave with an angular frequency, \( \omega \), through a metal.

\[
\varepsilon = 1 + \omega_p^2 \frac{\tau_e^2 + i \tau_e / \omega}{1 + \omega^2 \tau_e^2}
\]  

Equation 9

where \( \tau_e \) is the electron-ion collision time and \( \omega_p \) is the electron plasma frequency. The variation in optical properties with wavelength is dependent on the plasma frequency of a metal, \( \omega_p \), which describes the electronic oscillations along longitudinal modes. These modes cannot be directly excited by photons of light, which oscillate transversely, but can be excited indirectly through inelastic scattering. The plasma frequency, \( \omega_p \), is expressed as

\[
\omega_p = \sqrt{\frac{n_e e^2}{m_e \varepsilon_0}}
\]  

Equation 10

where \( e \) is the electronic charge, \( \varepsilon_0 \) is the dielectric constant in a vacuum, \( m_e \) is the electron mass. The frequency of the incident light, \( \omega \), relative to \( \omega_p \) will affect the material response, as the dielectric constant changes from negative to positive when the frequency of light increases through \( \omega_p \) [34]. If the incident laser light \( \omega < \omega_p \), the light will be reflected. If the incident laser light \( \omega > \omega_p \) the dielectric constant results in the transmission and potential absorption of the incident light. Metals characteristically have a \( \omega_p \) relating to a wavelength in the ultra-violet region and thus the metal will reflect light with visible wavelengths or longer, but transmit or absorb light in the UV. Bulk Au has a plasma wavelength and frequency of 138 nm and \( 2.18 \times 10^{15} \) Hz (9.01 eV), respectively [2, 34, 39].

For thin films, the optical properties are not represented by bulk values as they can vary with the film thickness and substrate optical properties. Figure 6 demonstrated the importance of considering the substrate in laser ablation of thin films, since the attenuation depth can exceed the thickness of the film. Therefore interference due to reflections at the film/substrate interface must be accounted
for in calculations. Heavens explored the contributions of the thickness and refractive indices of the film and substrate to calculation the reflection, transmission and absorption by a multilayer system [38]. Computational programs have since been designed to calculate the optical properties of films based on film thickness and optical data and have been shown to be in good agreement with experimental data.

2.3.3 Electronic Heating

The incident laser energy is primarily absorbed by the conduction band electrons in metals in a process called inverse Bremsstrahlung. The laser intensity penetrates into the material to a depth defined by the optical penetration depth, $\alpha^{-1}$, and the electrons within this volume absorb the laser energy and increase in temperature. Electrons have a relatively low heat capacity and thus reach in excess of $10^3$ K, whilst the lattice remains effectively cold [40]. The energy absorbed by these electrons is then dissipated during three stages:

The first stage describes a non-equilibrium state, during which two competing process ensue; One is the ballistic motion of excited electrons that penetrate deep into the material, at close to the Fermi velocity ($\sim$1000 km s$^{-1}$). The depth of the ballistic electron has been determined experimentally for Au as $\sim$100 nm, which was also comparable to the calculated mean free path of an electron (117 nm) [41]. This ballistic electron movement is significantly larger than the optical penetration depth for s- and p-band metals [27]. The other process occurring is that the excited electrons collide inelastically with electrons at the Fermi level. These electron-electron collisions dissipate the thermal energy between electrons in a relaxation process called electron thermalisation. The relaxation time, $\tau_{ee}$, describes the time for the excited electrons to relax into a Fermi distribution, which in metals typically lasts 10-100 fs [42]. The rate of electron thermalisation is dependent on the number density of electrons, their cross-section and their relative velocity [43, 44]. Elastic scattering rates of excited electrons is increased by defects impurities and grain boundaries, but these factors do not affect the inelastic scattering rate.
The second stage is where electron thermalisation has been reached, but the overall electron temperature is relatively ‘hot’ compared to the ‘cold’ lattice. These ‘hot’ electrons are localized within the ballistic electron range. Due to the steep temperature gradient between electrons and lattice, the electrons can continue to diffuse deeper to a length named the thermal diffusion length, but this diffusion occurs at a much slower speed than ballistic motion. The electron thermal penetration depth is based on the electron thermal diffusivity and the electron effective relaxation time. Au has a relatively high thermal conductivity of 317 W m$^{-1}$ K$^{-1}$ at 300 K compared to other metals [45] with the thermal penetration depth extending to over 700 nm [45].

The third stage of energy dissipation by the electrons is via the coupling of the energy from the electrons to the lattice via electron-phonon coupling, which will be described in more detail in Section 2.3.4.

The values of the optical, ballistic and thermal penetration depths should be considered relative to the film thickness. If the film thickness is less than any of these penetration depths, the laser energy can be effectively confined by the film thickness ($z$) and the laser beam diameter ($xy$), assuming that the substrate is transparent to the laser wavelength and has a low thermal conductivity. This has been shown to result in more uniform heating of the film [46].

### 2.3.4 Lattice Heating

Following electron thermalisation, the electrons are said to reach a uniform electron temperature, $T_e$. At this time, the lattice remains unheated and can be effectively described as ‘cold’ compared to the ‘hot’ electrons. The ‘hot’ electrons cool via the emission of phonons in a process termed electron-phonon coupling. For laser pulse durations that are longer than the electron thermalisation time, $\tau_{ee}$, but are shorter than the electron-phonon coupling time, $\tau_{ep}$, the material can be effectively described by the Two-Temperature Model (TTM) developed by Anisimov [47]. Anisimov described the electrons and
lattice as two separate systems and modeled their temperature response with the TTM. The model provides two coupled non-linear differential equations, which describe the energy transfer between the electrons and lattice as shown in Equations 11 and 12.

\[
C_e(T_e) \frac{\delta T_e}{\delta t} = \nabla [K_e(T_e) \nabla T_e] - G_{ep}(T_e - T_l) + Q(z,t) \quad \text{Equation 11}
\]

\[
C_l(T_l) \frac{\delta T_l}{\delta t} = \nabla [K_l(T_l) \nabla T_l] + G_{ep}(T_e - T_l) \quad \text{Equation 12}
\]

where \( C \) and \( K \) are the heat capacities and thermal conductivities, respectively, of the electrons (subscript \( e \)) and of the lattice (subscript \( l \)). The electron-phonon coupling term is represented by \( G_{ep} \), and the Source term, \( Q(z,t) \) describes the laser energy deposited into the electronic system by the laser pulse in space and time and follows the Beer-Lambert absorption law. The electron-phonon coupling term, \( G_{ep} \), is expressed as:

\[
G_{ep} = \frac{\pi^2 m_e C_s^2 n_e}{6 \tau(T_e) T_e} \quad \text{Equation 13}
\]

where \( m_e \) is the electron mass, \( C_s \) is the speed of sound, \( n_e \) is the electron density and \( \tau(T_e) \) is the electron relaxation time [48]. The rate, at which, the laser energy is coupled from the electrons to the lattice is described by the electron-phonon coupling term, \( G_{ep} \). The hot electrons couple their energy to the relatively cold lattice when they scatter off the lattice imperfections. The high frequency oscillations of the electrons interact with the lattice phonons and result in a change in the momentum of the electron and transfer energy to the internal energy of the lattice [43]. This then results in an increase in the temperature of the lattice.

Electron-phonon coupling times, \( \tau_{ep} \), in metals are typically of the order of a few picoseconds, but measurements made for nanosized metals show a reduction in this time [40]. This reduction in \( \tau_{ep} \) is likely to be due to the increased surface-to-volume ratio and therefore enhanced electron-surface scattering. The reduction in \( \tau_{ep} \) is also observed for highly crystalline Au, where a high density of grain boundaries increases scattering [49]. For Au films, Hohlfeld et al. showed that
$G_{ep}$ is approximately $2.2 \times 10^{16}$ W m$^{-3}$ K$^{-1}$ [41] and $\tau_{ep}$ is the inverse of this rate and typically takes place over several picoseconds [40]. Alternatively, it has also been shown to take far longer, up to 50-100 ps [50].

Following electron-phonon coupling, the temperature of the lattice rises and phonon-phonon interactions ensue after approximately 100 ps in Au [51]. Phonon-phonon interactions occur via scattering and results in heat conduction throughout the lattice to the depth of the thermal penetration depth of the material. If the temperature of the lattice is raised above the melting, boiling or sublimation temperatures, phase changes will occur on timescales of 300 ps – 1 ns, during or after which, ablation may also result.

### 2.3.5 Computational Modelling

Various computational models have been developed to predict or understand the mechanisms of laser-material interactions. With the escalation in computing power, these models are becoming increasingly complex and therefore producing more powerful insights. The development of the TTM was vital in the understanding of the response of electronic and lattice systems during femtosecond laser pulse absorption. However, as with all models, the impact of their assumptions and limitations are not always clear until further models and experimental studies are carried out. For example, the TTM does not account for the ballistic transport of electrons in metals, which has been shown to have a significant impact on the uniformity of material heating [41]. Recently, Amoruso developed the source term in the TTM to account for the increased penetration depth due to the ballistic motion of electrons in Au [52].

Importantly, the TTM also does not account for the following two details:

- The electron distribution function takes a finite period to achieve thermal equilibrium following $\tau_{ee}$ and therefore the electron temperature cannot be represented by a single temperature, $T_e$, for time-scales shorter than 1 ps.
- The electron-phonon coupling factor is not a constant
These assumptions are described by the emerging research area of Non-Equilibrium Dynamics (NED) in metals following ultra-short laser pulses \cite{48, 53}. Computational studies that incorporate NED have in fact shown that the electron distribution function is in thermal non-equilibrium for up to 1 - 2 ps following a femtosecond laser pulse \cite{54}. Although $\tau_{ee}$ occurs on a femtosecond time scale, the distribution function of electrons is in non-equilibrium for up to picoseconds due to the generation of secondary electrons \cite{53}. For this reason, the TTM cannot reasonably be applied for time-scales shorter than a few picoseconds. Additionally, the electron-phonon coupling factor, $G_{ep}$, has been shown to vary significantly when the density of states (DOS) of the material and the temperature dependency of collisions are accounted for \cite{53}.

By accounting for NED, computational models have identified significant differences in the material response to ultra-short pulses, particularly for noble metals. The accurate modelling of NED requires the incorporation of the temperature dependent electron density of states. To achieve accurate modelling of the laser-material interaction, the TTM model is continuously being improved by combining more mathematical descriptions of various elements of the laser heating process. Recent models that include NED will often utilise the following:

**Molecular Dynamics:**

Simulations use statistical mechanics to include interactions between atoms. Therefore this classical model does not explicitly include the contribution of electrons to the heating of the lattice.

**Atomistic model:**

Uses a finite body of atoms and measures the interactions between them e.g. Lennard-Jones potential.

**Continuum model:**

Ignores common defects of a crystal structure and assumes smooth and elastic deformations of atomic positions based on Bravais lattices.

**Density Functional Theory**

Quantum mechanical molecular dynamics model to describe electronic structures in different systems. E.g. Vienna Ab Initio Simulation package (VASP)
2.4 Laser Ablation Mechanisms

This section provides an overview of laser ablation, with particular focus on the mechanisms and the factors that govern them. It should be noted that this section only discusses the more prominent ablation mechanisms commonly discussed in the literature for the laser ablation of metals and thin films.

The mechanism of material ejection or laser ablation is dependent on both the materials chemical and physical properties, such as melting temperature and electronic structure and also on laser properties, such as pulse duration and laser fluence. In order for laser ablation to ensue, the material must be de-stabilized; it has been calculated that the absorption of photons induces a free carrier plasma when approximately 10% of the valence band electrons are removed and the bonding orbitals in the lattice are weakened [55]. The laser ablation threshold fluence, $\phi_{th}$, is a useful measure of the fluence required to cause ejection of material. However, in the literature, $\phi_{th}$ is expressed as the applied laser fluence, rather than, the absorbed laser fluence.

The ablation mechanism is dependent on the method and speed of energy dissipation by the material following the absorption of laser energy by the electrons. An increase in the incident laser fluence means that there is a greater quantity of energy for the material to dissipate, which can impact what ablation mechanism, ensues. The dissipation of energy throughout the volume can result in any combination of thermal/non-thermal excitations, phase changes, defect formation, temperature and volume changes etc. Ultra-short laser pulses can deposit enormous intensities of laser light into a material and result in non-linear material responses, not observed at longer pulse durations [56]. For femtosecond laser pulses, the dissipation of energy in the material and subsequent ejection of matter ensues after the termination of the laser pulse.

Ablation mechanisms are typically highly complex with many contributing factors but two categories are used to best encompass the main features triggering the onset of material ejection: photophysical and photomechanical ablation mechanisms.
2.4.1 Photophysical Ablation Mechanisms

Photophysical mechanisms encompass ablation that have both photothermal and photochemical contributions [57]. Photochemical ablation describes when absorption of laser energy results in direct bond-breaking. Photothermal describes ablation mechanisms resulting from a temperature rise of the material following laser absorption. Photothermal ablation mechanisms typically occur for ultra-short pulses and relatively low fluences, whereas higher fluences induce phase changes and more complex dynamics i.e. photophysical mechanisms. However, the ablation mechanism is rarely considered to be purely photothermal or photochemical alone, and photophysical mechanisms are far more commonplace.

The time-scale, on which photophysical laser ablation occurs was described effectively by the illustration by Kautek and is shown in Figure 7. The figure illustrates the initially non-thermal responses by the material on ultra-short times scales, before thermal processes develop that can induce phase changes.

![Figure 7: Ultrafast laser excitation of solids – Time-scale of material response. Figure by Kautek [51].](image-url)
The following photophysical ablation mechanisms have been observed for thin films:

a) Vaporisation
b) Phase Explosion
c) Coulomb Explosion

a) Vaporization

Vaporization of a material describes the phase transition from the liquid phase to a gas phase and can ensue by either evaporation or boiling. The transfer of the laser energy to the lattice via the electrons results in a rise in its temperature. If the melting temperature of the material is exceeded, a phase change from solid to liquid will occur. Vaporization of a liquid is described as binodal according to the pressure-temperature phase diagram i.e. the binodal curve represents the transition from saturated liquid to saturated vapour.

Heterogeneous Evaporation

Heterogeneous evaporation begins when the vapor pressure of the ambient gas around the target is less than the saturation pressure of the liquid. The saturation pressure of the liquid increases with temperature until molecules begin to transfer from the high concentration of the liquid surface to the low concentration in the gaseous vapour. With this process only the atoms/molecules nearest the target surface are involved with evaporation and the surface temperature decreases following evaporation.

Heterogeneous Boiling

Heterogeneous boiling occurs when the lattice is heated quickly to a temperature above the material boiling point. On boiling, nucleation of vapor bubbles occurs throughout the volume of heated material. Nucleation sites of gas or vapor bubbles typically occur at defects within the material e.g. solid/liquid interface. Growth of these bubbles occurs when the temperature of the nucleation size exceeds the saturation temperature of the liquid. This
mechanism is typically associated with longer laser pulse durations. Ejected species via this mechanism typically have similar kinetic energy and the temperatures will be near the vaporization point [58].

b) Phase Explosion (Homogeneous nucleation)

This mechanism is modeled largely on classical thermodynamics and describes when the surface region is heated so quickly that it exceeds the boiling point of the material and is said to become superheated. A superheated material has exceeded the limit of its thermodynamic stability, but can still be metastable. However, if the liquid reaches the spinodal limit, the liquid becomes highly unstable. At this point the liquid decomposes spontaneously into a phase, in which the liquid and vapor phases coexist. In some cases, the spinodal is not reached due to the onset of homogeneous nucleation. In this case, vapor bubbles are spontaneously created throughout the liquid, without requiring nucleation sites. This homogeneous nucleation of bubbles grow and reach a critical size whereby the material is classed as a liquid-gas mixture and the expansion proceeds in an explosive way. This leads to the rapid transition from a metastable superheated liquid into a mixture of vapor and liquid droplets and is described as a phase explosion [59, 60]. This is typically the mechanism most associated with laser ablation and has been used to explain a sharp increase in observed ablation rates occurring at high fluences [61].

c) Coulomb Explosion

Ultrafast ablation mechanisms, such as Coulomb Explosion, occur before thermalisation between hot electrons can take place. The ejection of electrons via photoemission or thermionic emission occurs on very short time-scales and results in unshielded positively charged ions within the lattice. If the repulsive force between these positively charged constituents exceeds the lattice binding energy, the material explosively breaks up [43].

Characteristic evidence of the Coulomb Explosion ablation mechanism is that there are two distinct velocity regimes of electrons: fast (energy order of eV) and
slow electrons (energy of meV) [62]. Other evidence includes the smooth surface that remains following the explosion of material during this mechanism [63].

Coulomb explosion is an ablation mechanism commonly observed for dielectrics and some semiconductors, but its applicability to the ablation of metals remains controversial. Some studies assume that Coulombic Explosion does not occur with metals due to their high electron mobility and effective screening of positive charges [58, 62]. However, there are a few studies that provide evidence to the contrary [64]. Mafune found that multiple nanosecond laser pulses of Au nanoparticles in a liquid resulted in the emission of large numbers of electrons and left the nanoparticles highly charged [65, 66]. The observation of nanoparticles fragmenting into smaller nanoparticles was attributed to Coulomb explosion. This evidence and theory was also supported in the femtosecond laser regime by Meunier et al. [67].

Single pulsed Coulomb Explosion may also be more feasible for thin metal films, where the electron mobility is restricted in the z direction by the thickness of the film and the substrate. Electrons ejected from the ablated volume must be replenished by electrons in lateral positions to the ablated volume. Additionally, the resistivity of thin film metals is far greater than for the bulk equivalents.

### 2.4.2 Photomechanical Ablation Mechanisms

Photomechanical ablation describes mechanisms that occur due to the build up of mechanical stress in a material following laser absorption. The build up of stress/strain in a material can occur from thermal or non-thermal effects and are named thermomechanical or photomechanical, respectively [57]. The process is typically photomechanical when the material relaxation time is shorter than the pulse duration.
This section briefly describes the following ablation mechanisms:

- **d) Delamination**
  Delamination is a photomechanical ablation mechanism associated with thin films. The laser heating of the thin film causes a steep temperature rise causing the film to expand away from the substrate below. This fast expansion can cause mechanical stresses to build in the film, which ultimately causes the film to fracture or blister in a process called delamination. This expansion away from the substrate is exacerbated when the substrate has a low thermal expansion coefficient compared to the thin film.

- **e) Spallation**
  Spallation is a non-thermal mechanical ablation mechanism. The absorption of a laser pulse induces a compressive stress pulse that propagates from the surface to the film-substrate interface before reflecting and becoming a tensile wave. The compressive stress is generated since the film temperature rises quickly and the film expands. The amplitude of the tensile wave is dependent on the absorbed fluence and if the tensile shockwave exceeds the tensile strength of the material, the material is mechanically destabilised and spallates [68]. This mechanism requires that the tensile wave is generated prior to phase changes in the material, which is not always feasible at very high fluences [69]. Typically, the target heats to a supercritical state during this mechanism, but remains in the solid phase before cooling down to below the triple point and finally results in a solid-vapor transition following spallation of material.
f) Thermoelastic ablation

The absorption of ultra-short laser pulses can induce the rapid build-up of thermoelastic stress in the material. When the electron-phonon coupling time is shorter than the time required for thermal expansion (Au $\sim$ 5 ps), the stress confinement results in large thermoelastic pressures in the material. Stress confinement is particularly strong in thin films and can result in very high thermoelastic pressure which then culminate in spallation or void formation [57].

g) Fragmentation

Fragmentation is a thermal mechanical ablation mechanism and occurs at higher energies than spallation. Stress in the material builds due to the constant expansion and the internal stress is converted to strain before becoming a supercritical fluid, which fragments into liquid drops. During this fragmentation, the strain energy in the material is converted into surface energy for the liquid fragments. Excess elastic energy stored in the target can exceed the surface energy of the target, in which case the excess elastic stress is converted to surface energy during the formation of the fragments.

2.5 Plasma and Plume Generation

During laser ablation, electrons, ions, atoms and particles can all be ejected from the target material. The ejected components that are charged, such as electrons and ions, are described as the plasma. The neutral components that are ejected, such as atoms and particles are described as the plume. The ejection of the plasma component typically occurs up to tens of picoseconds [60] with the emission of nanoparticles occurring up to several hundred nanoseconds after the laser pulse for ultra-short laser ablation [60]. The exacting time-scale on which the electrons, atomic and ionic mass is ejected is highly dependent on the mechanism for ablation. The mechanism for ablation is highly dependent on the combination of laser and material properties.
2.5.1 Electron Emission

The incident laser energy is absorbed by the electronic system and can result in the ejection of electrons by either Photoelectric or Thermionic photoemission. Both mechanisms are dependent on the electron temperature and the work function of the material. In the case where a single laser photon has insufficient energy to exceed the work function of the material, it is possible for multiple photons to be absorbed by a single electron, thus resulting in its ejection. This mechanism is named Multiphoton Photoemission (MPPE).

Studies have shown that the electrons in the surface of a metal target reach temperatures on the scale of $10^4$ K and this temperature increases slowly with increasing laser fluence [70]. The electrons that are ejected from the material form part of the plasma and these electrons can reach much higher temperatures, on the scale of $10^5$-$10^6$ K. Unlike ions, the temperature, velocity and flux of these electrons are only weakly dependent on the angle [71].

Previous investigations into the effect of laser wavelength on the formation of an aluminium plasma showed that the laser irradiance required to form a plasma was much higher at 1064 nm, than for 532 nm and 355 nm [72]. However, the reflectance of the sample was unaccounted for and could be responsible for this effect.

The two dominant emission mechanisms for electrons in this study; Multiphoton Photoemission and Thermionic emission, are explained in this section.

Multiphoton Photoemission (MPPE)

The photoelectric effect was first observed by Einstein in 1905 and was a key discovery en-route to establishing the theory of quantized energy. An electron is emitted from a target when the electron has absorbed a quantity of laser energy that is sufficient to overcome the work function of the material [73]. This can be achieved by the absorption of a single photon or multiple photons simultaneously.
or sequentially. Therefore this mechanism occurs within the duration of the laser pulse.

The likelihood of the non-linear Multiphoton Photoemission (MPPE) process occurring is described by the absorption cross-section, \( \sigma_n \). The electron emission rate, \( J_n \), is proportional to \( I^n \), where \( I \) is the incident laser intensity and \( n \) is the number of photons absorbed [73]. The absorption of an increasing number of photons requires exact phase and time matching of all the photons and this consequently reduces \( \sigma_n \). For this reason, the MPPE process is substantially more recurrent with photons of higher energies (lower wavelengths), as fewer photons are required to be absorbed to exceed the work function. It is also possible to have thermally assisted MPPE, whereby photons are sequentially absorbed and the work function is exceeded during the pulse duration [74].

The energy of the electrons emitted does not depend on the laser intensity, but the energy of the photon. The absorption of a photon or of multiple photons provides the energy to overcome the work function and the excess contributes to the kinetic energy of the electron once liberated from the material. Therefore the maximum kinetic energy of MPPE electrons is \( E_k = n\nu - W_F \), where \( n \) is the number of photons required to be absorbed to initiate MPPE and \( W_F \) is the work function of the metal.

**Thermionic Emission**

The partially competing process to MPPE of electrons is thermionic emission. Thermionic emission occurs when sufficient thermal energy induces charge carriers to overcome the work function of the material. Therefore thermionic emission can occur on longer time-scales than MPPE, extending beyond the end of the laser pulse. As the electrons absorb the incident laser energy, the Fermi-Dirac distribution of electron energies is altered and the electrons at the Fermi edge move to higher energy states, as illustrated by Figure 8.
The current that is generated by the thermally emitted electrons from a metal, $J_T$, is described by the Richardson-Dushman equation [75].

$$J_T = A T_e^2 e^{(-W_F/k_BT)}$$

Equation 14

where the Richardson coefficient, $A$, can be calculated for Au:

$$A = \frac{4 \pi m_e k_B^2 e}{\hbar^3} = 1.20173 \times 10^6 A m^{-2} K^{-2}$$

Equation 15

2.5.2 Atomic and Ionic Mass Emission

The atomic and ionic component of the plasma plume typically constitutes a very low fraction of the total ablated material (10-20%), whereas the nanoparticles dominate the plasma plume composition [4, 76]. The ejected electrons and ions are initially coupled and the peak ion and electron temperatures temporally match, but then decouple after a few mm [71]. However, the ion temperature is several orders of magnitude greater than the electron temperature due to the greater heat capacity [71].
The formation of ionic masses can occur via two pathways. Firstly, the ejection of electrons from the target surface can result in a layer of positively charged Au ions at the surface, which is highly unstable and can effectively be torn away due to the electric field. Alternatively, at high fluences, neutral atomic species can be ionised following ejection. The species in the plasma plume are dependent on the ablation mechanism and potentially any reactions of these species with the ambient medium [57].

The propagation of a laser generated plume has been monitored using shadowgraphy and optical spectroscopy. Itina and Noel determined that the velocity of Au ions, Au atoms and Au nanoparticles were 10 km/s, 1 km/s and 100 m/s, respectively [77]. Amoruso et al. compared the plume generated from a 100 nm thin film and bulk Au [46]. Amoruso found that the plume propagates in two components. The plume detaches quickly from the film but the emission of the plume from bulk Au remains attached to the surface for a longer period. It was found that the velocity of the nanoparticles ejected from a thin film travelled at 400 m/s compared to 130 m/s from bulk Au.

2.5.3 Plasma Expansion

The initial velocity of species ejected from a surface is typically of the order of 1 – 10 km/s, from which it can be inferred that no plasma plume develops during the duration of the femtosecond laser pulse [57]. Laser ablation in a vacuum will typically result in a plasma that initially expands at a supersonic velocity [5]. The propagating vapour moves from a non-equilibrium to an equilibrium distribution over a distance called the Knudsen layer. The Knudsen layer describes the region above the surface, in which the species thermalise via collisions and achieves a Maxwellian distribution. The Knudsen layer typically stretches over a few mean free paths from the surface [57]. Within this layer, a steep temperature and pressure gradient exists perpendicularly to the surface and causes the plume to expand quickly upwards along the surface normal. Collisions occurring within the Knudsen layer results in a more forward peaking plume.
After the femtosecond laser pulse terminates, the gaseous layers of the target expand in all directions away from the target surface. This expansion is driven by the absorption of laser energy redistributed firstly as thermal energy and then to kinetic energy of the electrons, ions, atoms and molecules in the plasma plume [78]. In a vacuum, the plasma can expand freely and reaches a final constant velocity and can therefore be described by the adiabatic equation of state; whereby the entropy is constant, and the $P_p / n_p \gamma = \text{constant}$, where $P_p$ is the plasma pressure, $n_p$ is the plasma density and $\gamma$ is the specific heat ratio ($C_p / C_v$) [57]. The specific heat ratio indicates how much the plasma temperature increases as it is compressed.

The ejected electrons and ions are coupled to each other via the Coulomb field and therefore exchange energy through collisions until the plasma is equilibrated. As the plasma expands adiabatically into the vacuum, the plasma cools.

**Plasma Dimensions**

The expansion of a laser plume has been theoretically described by Singh and Narayan [79] and then Anisimov [80, 81]. Both describe the adiabatic expansion of a small volume of hot gas into a vacuum [82]. Singh and Narayan describe the expansion as isothermal, whereas Anisimov describes the expansion as isentropic. Within the literature, the Anisimov model is typically favoured as it can also be applied to the plasma expansion [82] and nanoparticles [4].

Anisimov describes the plume expansion as semi-ellipsoid where the density and pressure are constant on all ellipsoidal surfaces. The model defines the initial plume dimensions with the radius, $R_0$ approximated by the laser beam radius and the initial height of the plume, $Z_0$ as approximately equal to $Z_0 \approx v_s \tau_p$ where $v_s$ is the velocity of sounds and $\tau_p$ is the laser-pulse duration [81]. The position of the particles in the plume is described relative to the plume front. Anisimov determines that the plume temperature decreases with distance from the surface [81]. In the case of laser ablation in a vacuum, the shape and velocity distribution of the plume will reach asymptotically constant values [78].
When examining laser ablation of material and plasma formation, it can effectively be described by the adiabatic limiting case, in which the laser absorption, heating, vaporisation and plasma formation all occur before the expansion of ablated material away from the surface [83]. This assumption results in the ablation process occurring during two stages. The first stage is the evaporation of the solid target and the formation of a plasma. The second stage is the expansion of the ablated vapor cloud into the ambient. This assumption simplifies the process, whereby the incident laser energy is first converted to internal energy of the target and vapor cloud and is then converted to kinetic energy of the ablated matter. The Anisimov model suggests that the angular distribution of the plasma is dependent on the initial dimensions of the plasma and the adiabatic index, \( \gamma \). Adiabatic index, \( \gamma \), is the heat capacity ratio at constant pressure and volume and is also known as the isentropic expansion factor. There is further information regarding the Anisimov model for plasma plume expansion in Appendix A.

A recent study by Lunney built on this isentropic, adiabatic gas dynamical model of plume expansion for laser ablation in a vacuum [82]. The exact plume dimensions are dependent on the initial plume dimensions and the background gas pressure. At low pressures (<10\(^{-3}\) Torr) the plume accelerates over a few millimeters before expanding inertially with little effect by the background gas.

**Space-Charge Field**

In a bulk plasma electrons accumulate around a positive charge, thereby shielding it from the electric field. A fundamental property of a plasma is the distance, over which the electric field is shielded from such a charge and is named the Debye length, \( \lambda_D \). Beyond this length the charge is fully shielded and therefore the local electric field is zero.

\[
\lambda_D = \sqrt{\frac{\varepsilon_0 k_b T_e}{e^2 n_e}} = 7.43 \times 10^3 \sqrt{\frac{T_e}{n_e}}
\]

Equation 16

Following the absorption of pulsed laser light the emitted electrons propagate away from the surface with high kinetic energies, whereas the higher mass ions
propagate at lower velocities due to their differing relative masses. A cloud or electrostatic sheath at the front of the plasma plume comprising of electrons acts to accelerate the ions away from the target surface. This separation of charges and acceleration of ions by the electrostatic sheath is named the Space-Charge effect. The ions and electrons are coupled to each other through Coulomb fields and exchange energy via collisions until the charges are neutralised. The kinetic energy of the ions is therefore directly proportional to the hot electron temperature.

The electrons at the front of the expanding plasma can also interact with other electrons leaving the target surface at a later time and can either accelerate them [84] or drive these electrons back to the surface. Space-Charge effects have been shown to suppress thermionic emission of electrons and produce a yield that varies linearly with temperature [74]. Interpretation of time-of-flight data for plasmas must therefore include consideration of these interactions between the plasma components following their ejection.

2.5.4 Langmuir Probes

There are many optical and electrical techniques that have been used to examine the plasma plume and their features have been discussed in detail by Amoruso [83]. Langmuir probes are a useful, inexpensive tool for measuring the properties of a collisionless steady-state expanding plasma. Such properties include the plasma shape, velocity, density and temperature. Although the probe itself is a simple tool to implement, the analysis of the data brings numerous complexities that have resulted in a plethora of papers discussing the appropriate interpretation of data.

The analysis of time-of-flight (TOF) data collected with Langmuir probes assumes that the velocities of the ions and electrons can be described by Maxwellian distribution functions. A useful overview of the application of Langmuir probes to laser ablated plasma plumes was given by Doggett and
Lunney, who discuss the importance of probe dimensions, appropriate techniques and accurate interpretation of results [5].

Distinction between the different plasma species by a Langmuir probe is possible due to the bias voltage applied and the fact that different species travel at different velocities. It should be noted that the Langmuir probe offers no way of measuring the neutral component of the plasma, such as atoms, molecules and nanoparticles and other methods would be required to measure these e.g. mass spectrometry. When a voltage bias is applied to the probe, the net current drawn by the probe is due to the flux of charges. If the bias voltage, $V_B$, is varied from negative to positive, different species will be detected at the probe, resulting in a variation in the measured current, $I$. The current, $I$, generated by the flux of positive ions on a negatively charged probe is given by:

$$ I = A e n_i v_i $$

Equation 17

where $A$ is the probe area, $e$ is the electron charge, $n_i$ is the number density of ions and $v_i$ is the ion velocity [85]. Druyvesteyn determined that the second derivative of the probe current with respect to the voltage bias at the probe was proportional to the electron energy distribution function (EEDF) [86]. The number and type of charged species impinging on the Langmuir probe is dependent on the bias voltage applied. Measuring the current during a sweep of different bias voltages generates a characteristic IV graph that can be used to clarify a number of features of the plasma e.g. the electron temperature using the analysis set out by Koopman and Segall [87]. An example of an IV graph is shown in Figure 9 and each region is described in Table 2.
Figure 9: Characteristic IV graph. Current, $I$, generated for a sweep of bias voltages, $V_B$.

Table 2: The effect of the voltage bias on the charged species arriving at the Langmuir probe and contributing to the measured current. Effects shown for sweeping voltage bias from negative to positive.

<table>
<thead>
<tr>
<th>Ion Saturation Current</th>
<th>Negative $V_B$. Electrons are repelled and the positive ions are attracted to the probe. All the ions are being detected by the probe regardless of how much $V_B$ is decreased and hence the current generated by the ions, $I_i$, is effectively constant.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition Regime</td>
<td>Range of $V_B$ whereby both electrons and ions contribute to the overall detected current.</td>
</tr>
<tr>
<td>Floating Potential</td>
<td>The point at which the current generated from electrons, $I_e$, is equal to the current generated from ions, $I_i$. This therefore results in an overall detected current of zero.</td>
</tr>
<tr>
<td>Electron Saturation Current</td>
<td>Positive $V_B$. Electrons are attracted to the probe and positive ions are repelled. All the electrons are being detected by the probe regardless of how much $V_B$ is increased and hence the current generated by the electrons, $I_e$, is effectively constant.</td>
</tr>
</tbody>
</table>

Under ideal conditions the electron saturation region, shown in Figure 9, is level, however, a sheath forms around the probe that can result in a steep plot in the electron saturation region. The shape of the IV plot is also dependent on the shape of the probe [88]. The transition region only measures the electrons with sufficient kinetic energy to overcome the plasma potential. The plasma itself is
quasineutral, however, the plasma potential, $V_p$, is typically slightly positive due to the higher mobility of electrons relative to ions. When $V_B$ is zero, the expected current would also be zero since the current contributed by both the ions and electrons should cancel each other out. However, since the electrons reach the probe first, a plasma sheath forms around the probe. The plasma sheath refers to the spatial potential profile between the bulk plasma and the probe surface, in which an electric field exists typically over a few Debye lengths. This sheath forms around the probe surface due to the difference in the plasma voltage, $V_p$, to the bias voltage, $V_B$, in an attempt to maintain charge neutrality in the bulk plasma. Therefore the sheath expands with increasing bias voltage. A higher number of electrons detected by the probe in the transition region indicates a greater $V_p$.

**Probe Dimensions**

The detection of electrons emitted by metals following pulsed laser absorption using a Langmuir probe have often been shown to deviate in number and kinetic energies from theoretical calculations. The explanation for this deviation is attributed to space-charge effects in the electron cloud [84].

However, these collisions are considered negligible if the plasma is highly ionised and the mean free path, $l$, exceeds the Debye length, $\lambda_D$, is greater than the probe dimensions, $A$ [89]. Typical Debye length within this setup would be 24 µm compared to the Langmuir probe diameter of 1.2 mm. If a charged species is added to a plasma that perturbs the overall charge neutrality, there is a characteristic length over which the plasma charges will move to shield the electric field generated by the addition of this charged species. This characteristic length is termed the Debye length, $\lambda_D$ as described in Equation 16. In order to measure the quasi-neutral plasma, the size of the Langmuir probe tip should exceed the value for $\lambda_D$. 
2.6 Nanoparticle Generation

During laser ablation of material, the ejected debris is typically nano-sized and are therefore termed nanoparticles. The nanoparticles are effectively the debris of the ablation mechanism and therefore their, size, shape and number can provide insight into the ablation mechanism.

The mechanism of nanoparticle formation is still poorly characterised and varies depending on a number of factors. The time-scales, on which the processes take place are so short that until recent advancements in ultra-short metrology, most studies have used computational models to predict the evolution of nanoparticles. This section summarises the theory of the formation and evolution of these nanoparticles that is presented in the literature.

2.6.1 Nanoparticle Formation

The phase, size and shape of the primary particles ejected during laser ablation are highly dependent on the ablation mechanism of the target material [90]. For example, the nanoparticles can form directly from the target material via mechanical mechanisms, whereby solid fragments or clusters break away. The nanoparticles can also form when the target material melts and liquid droplets are ejected. Alternatively, the target material is vaporised and the nanoparticles then form in the expanding plume by thermodynamic nucleation.

For a nanoparticle to form, it must exceed a critical radius, \( r_c \), in order to be deemed thermodynamically stable. The \( r_c \) of nuclei is the minimum radius of a cluster of atoms, above which, the cluster is stable enough to exist and grow i.e. beyond this radius the formation of the cluster is no longer reversible and the cluster is termed a nucleus. The \( r_c \) of a spherical nucleus under isothermal conditions is expressed by:
where \( \sigma \) is the surface tension coefficient, \( V_n \) is the volume available per atom within the nucleus and \( \mu \) is the chemical potential for the metastable vapor and \( \mu_n \) is the chemical potential for the nucleus. \( S \) represents the degree of supersaturation and is a ratio of the partial pressure of the vapor, \( p \), divided by the saturation vapor pressure, \( p_s \). The partial pressure of the vapor is the pressure that the gas would exert if it occupied the volume alone. The saturation vapor pressure is a temperature dependent property of the liquid and determines how dense the vapor is above its surface in an equilibrium situation. The chemical potential is the change in system energy when entropy, number of other particles, surface area and volume are kept constant and one molecule is added to the system. i.e. sum of kinetic and interaction energies of one molecule. At chemical equilibrium, the total sum of chemical potentials is zero, as free energy is at a minimum.

Following the formation of the nanoparticles in the plume, their evolution is governed by collisions, their velocity and phase and the ambient environment. The nanoparticles ejected into the ambient can undergo collisions with one another during the plume expansion. Collisions between particles can lead to condensational growth resulting in uniformly larger particles or can lead to agglomeration or coalescence to form aggregates or larger particles. The number of collisions between particles is dependent on the number of particles and their velocities, e.g. if the particles have similar velocities, the collision rate is low. The outcome of these collisions is dependent on the nanoparticle phase and surface energies. According to the Young-Laplace equation, the stability of a droplet increases as the radius, \( r \), tends to infinity. Therefore it is more energetically favourable for particles undergo condensational growth or coalesce to form larger particles.
2.6.2 Factors affecting the Generation of Nanoparticles

The factors affecting the laser generation of nanoparticles will be discussed in three categories;

i) Laser parameters

ii) Material properties

iii) Ambient environment

i) Laser Parameters

At low fluences, it has been shown that thin films can be melted without ablation of material to form a nanostructured surface. Henley et. al. investigated the nanostructuring of thin metal films of 6-15 nm thicknesses on oxide substrates with up to 50 EXCIMER nanosecond laser pulses per area [91]. By melting the thin metal film, Henley achieved the reversal of the Volmer-Weber island growth, where the film melted and formed hemispherical islands on the oxide surface and was named EXCIMER Laser Nanostructuring (ELN) [92].

At higher fluences, ablation of the thin films can be achieved, during which nano-material is ejected from the substrate [93]. It has been shown that higher fluences result in a higher number of smaller nanoparticles, though this effect was also affected by the material [7]. This effect was attributed to the higher temperatures reached following the absorption of higher pulse energies, thus resulting in an increased cooling rate that favours the production of smaller nanoparticles. The effect of pulse duration has also been thoroughly investigated; shorter laser pulse durations result in the generation of a smaller average nanoparticle with a smaller size distribution [94].

The effect of laser wavelength on the generation of nanoparticles has been investigated, but primarily at a single laser fluence for all wavelengths [95-97]. This method does not account for the differing absorbed fluences by the material owing to the differing optical properties at different wavelengths. Hence the assumption in the study by Nikov et al. that the ablation of Au at 1064 nm wavelengths results in larger nanoparticles than at 355 nm and 532 nm, due to a
wavelength dependence, is more likely attributable to the lower fluence absorbed at 1064 nm than both 355 nm and 532 nm [95]. Currently, when considering nanoparticle generation during laser ablation, there is no standardized approach to the process of producing, collecting and measuring them.

ii) Material Properties

The confinement of the laser-material interaction by the thickness of a thin film can lead to the production of a much more uniform nanoparticle size, in comparison to from bulk materials [11, 46]. The non-uniformity of the thermal distribution evident in bulk materials leads to the ejection of material from different depths and with different energies, which results in a larger mean size of nanoparticle [11, 77]. Recent modeling studies have compared the thermal distributions, 40 picoseconds after a fs laser pulse, and found that the temperature varied by only 50 K throughout a 100 nm film compared to 1400 K over a 200 nm depth in the bulk Au [46]. This quasi-uniformity in Au films of 100 nm thickness is as a result of the motion of ballistic electrons in Au films, which can travel approximately 100 nm owing to the mean free path of an electron in Au calculated to be 117 nm [46]. The study presented in this thesis compared films of thicknesses within the ballistic electron depth, which according to this model would imply that the thermal distribution throughout films of 10 – 90 nm in thickness is quasi-uniform. Therefore the differences observed for nanoparticles generated from sub-100 nm thick films must be attributed to another factor.

In bulk materials, the temperature distribution across the target is non-uniform and can result in the ejection of hot particles with high velocities from the surface and slower, heavier particles from deeper in the material. This results in a high collisional rate and high numbers of clusters have been observed for metals [98]. This clustering effect is not as dominant for nanoparticle generation from thin films, since the particles are ejected from a uniformly heated material and therefore travel at similar velocities, minimising the collisional rate [46].
In a previous study, it was shown that nanoparticles generated from different materials, Au, Al and Ni films, with UV fs laser pulses increased in size, respectively [18]. The key properties contributing to these differences in nanoparticle size were the increasing electron-phonon coupling factor and surface energy of the material. During this review, no studies were encountered that investigated the relationship between the grain size of the material structure and the nanoparticles that were generated during laser ablation.

**iii) Ambient Environment**

The ambient environment, in which, the laser generation of nanoparticles takes place, can also affect the formation, growth and evolution of the nanoparticles. This section describes the impact of generating nanoparticles in either a liquid, a gas or in vacuum conditions.

**Liquid:** This is the favored environment for nanoparticle generation since it provides a suitable method of their collection and greater opportunity for nanoparticle stabilisation [13, 94]. Multiple laser pulses are typically applied to a bulk material submerged in a liquid and results in the uniform production of nanoparticles [16]. This method offers great versatility since the user has the choice of any liquid or surfactant to suit the end application of the laser generated nanoparticles. The stability of laser generated metal nanoparticles in a liquid has been attributed to their surface charge resulting in electrostatic repulsion between particles, which can overcome the need for surfactant stabilisation [7]. It has, until recently, been unclear whether the nanoparticles grew inside or outside of the cavitation bubble [99, 100]. Itina identified the influence of liquid properties, such as temperature, mechanical impedance and viscosity, on the shock wave and cavitations bubble formation, which in turn can affect the size of nanoparticles [101]. One key drawback of this method is the production time which can extend to multiple hours [94]
Gas: After several microseconds, the plume expansion is entirely determined by the interaction of the atoms and particles with the background gas atoms [78]. The gas therefore impacts the collisional rate between nanoparticles and also affects the heat dissipation from the plume, which can affect the condensational growth rate of the nanoparticles. At high gas pressures (> 0.1 mbar) the ablated plume broadens in distribution and is quenched leading to the homogeneous nucleation of the atoms and nanoparticles [52, 102]. High molecular weight gases with high internal energy can aid the fast cooling of nanoparticles, which lends itself to producing small nanoparticles [18, 102]. The rate of nanoparticle production has been shown to be ten times higher than nanoparticle production in a liquid [7, 13].

Vacuum: The production of nanoparticles in a vacuum facilitates the free expansion of the plasma plume. Therefore collisions between particles depend on the velocities of the particles ejected from the target material. The formation of aggregated clusters is more common in vacuum conditions than in an ambient gas [98]. The mean size of the nanoparticles produced in vacuum are typically smaller than those produced at higher pressures [46, 103]. The high mass ratio of nanoparticles to a background gas (relative to the plasma) results in nanoparticle plume expansion which is forward peaking and with only a slightly reduced velocity relative to plume expansion in vacuum conditions [104]. Without the contribution of the background gas to quenching, the nanoparticles remain molten and travel greater distances following ablation.

2.6.3 Techniques for Monitoring Material Ejection

The techniques used to explore nanoparticle generation during laser ablation typically take place offline. For laser ablation in ambient conditions,
nanoparticles are typically collected on a substrate and analysed most commonly with either Atomic Force Microscopy (AFM) or Scanning Electron Microscopy (SEM). Although these methods provide valuable information about the ejected material, there is increasing interest in optimising online metrologies to provide real-time information about the material ejection process.

The emission of the plasma, plume and nanoparticles from the target material during laser ablation has been monitored using a variety of methods discussed by Schou et al. [78]. One such method to monitor all of these components is to record the optical emissions from the plume using an intensified charge-coupled device (iCCD). The emissions from a target metal varies considerably with pulse duration [105] and with ambient environment [102, 106].

The plasma plume has been imaged and during ultra-short laser ablation, can be considered in three parts, the first part travels at 100-200 km/s, second component at 20-30 km / s and the last component travels at < 1 km/s [78]. The first component relates to the ions, second component to neutrals and ions and the slowest component to nanoparticles. The velocity of the emitted nanoparticles has also been shown to depend on the material thickness; Amoruso et al. compared the plume emission following fs 527 nm ablation of a 100 nm Au film with bulk Au [46]. The relative expansion velocities were found to be 370 m/s and 120 m/s, respectively. The nanoparticles ejected from the film and the plume quickly detached from the substrate, unlike from the bulk Au, where the nanoparticle plume remained in contact with the surface for several tens of microseconds.

It is also possible to combine plume imaging with optical emission spectroscopy to ascertain the chemical components of the plume. Spiga et al. used optical emission spectroscopy to analyse the chemical components of the plume [107]. The intensity of emissions was greatest at time-scales shorter than 100 ns. Spectral lines were observed for Au I at 583.74 and 627.82 nm. A blackbody continuum emission was observed for the plume on the microsecond time-scale and this was attributed to nanoparticles. The shift in the wavelength of this emission was attributed to the decrease in the temperature over time. The
nanoparticle emission intensity, $I(\lambda)$ can be considered as blackbody emission and therefore can be related to the nanoparticle plume temperature using

$$I(\lambda) \propto \lambda^{-5} \exp\left(\frac{hc}{\lambda k_B T}\right)$$

Equation 19

Therefore a plot of $1/\lambda$ against $(\log) I(\lambda)^5$ gives a line with a gradient equal to $hc / k_B T$, from which the temperature of the particles can be calculated [76]. The silicon nanoparticles (7 nm) generated following femtosecond laser ablation cooled at a rate of 15 K / µs at 10 µs, which slowed to 2 K / µs at 150 µs.

2.6.4. Schlieren Imaging

When light propagates through a homogeneous medium, the light is unperturbed. Inhomogeneity can arise from variations in gas composition, temperature and density, which affects the refractive index. These subtle variations in refractive index give rise to perturbations in the propagation of light, which are measurable using a schlieren imaging setup. In gases, the refractive index is proportional to the density of the gas.

$$n - 1 = k_{GD} \rho$$

Equation 20

where $k_{GD}$ is the Gladstone-Dale coefficient (0.23 cm$^3$/g for air in standard conditions). The observed refraction of light results from a variation in the gradient of the refractive index along a particular direction e.g. along a distance $L$ in the y direction, the angle of ray deflection, $\varepsilon$ is

$$\varepsilon = \frac{L}{n_0} \frac{dn}{dy}$$

Equation 21

Schlieren imaging can be achieved using a variety of setups using lenses or mirrors that are discussed in detail by Settles [108]. An incoherent light source is focused and collimated using a pair of lenses, with the light passing across the area of interest. The light is then focused and collimated by a second pair of lenses before a real image of the area of interest is formed on a CCD camera. The
details of the setup are discussed further in Section 3.7.1. Typically a matched pair of spatial filters are used in the two conjugate focal planes of the laser beam. The most favoured pair of filters is the Toepler slit and knife edge combination. A slit was first introduced by Toepler to enhance the sensitivity of imaging and defines the shape of the light source. The key component of the slit is that there is a straight edge that matches the straight edge of the knife-edge.

The slit and knife-edge are orientated perpendicular to the direction of perturbation in the interaction zone to maximise sensitivity. Therefore, the imaging of ablation plumes typically require the horizontal orientation of the slit and knife-edge. The knife-edge can then be orientated to block either the upper or the lower phase of the light. For the benefit of this study, the knife-edge is considered as horizontal and orientated to block the lower portion, unless otherwise stated. When a schlieren object is positioned in the collimated light zone, the light is caused to refract and a portion of light no longer focuses at the point on the knife-edge. If the light is reflected upwards, the light will be incident on the CCD and a bright spot will be imaged. If the light is reflected downwards, the light will be blocked by the knife edge and a dark spot on the CCD will arise. This refraction of the light results in a schlieren image of the object forming at the CCD.

When the knife-edge is positioned to block 50% of the light, it will result in a dark image, and is described as dark field imaging. If the knife-edge is adjusted slightly from this position, the image is described as bright field imaging. Optimal sensitivity using a knife-edge has been found when the knife-edge blocks 85% of the unperturbed light.
2.7 Section Summary

This review has assessed many studies within this research area and has highlighted some gaps in the literature. For example there is scope for direct comparison studies between different laser parameters, such as fluence and wavelength, if the optical properties are accounted for. In terms of laser ablation of materials, the grain microstructure has only been considered briefly in modeling terms with respect to its influence on the movement of the electrons within the material. With the fabrication of films with different microstructures in this study, this material property can now be investigated experimentally in relation to the size correlation of the grains with nanoparticles produced during laser ablation. In summary this review has highlighted the need for studies such as this one that probes the fundamental science behind laser ablation, thin film microstructures and nanoparticle generation.
Chapter 3
Equipment and Methods

This chapter details the fabrication and characterisation of thin Au films followed by the experimental techniques and analysis for plasma and nanoparticle generation during femtosecond laser ablation. Section 3.1 outlines the fabrication of the thin Au films and describes the applied parameters. Sections 3.2 and 3.3 explain the various techniques used to characterize the physical and optical properties of the sets of thin Au films, respectively. Section 3.4 describes the femtosecond laser setup, including typical values for the laser parameters and also how different properties are calculated. Section 3.5 details the techniques used to characterize the nanoparticles that are generated during laser ablation. Finally, section 3.6 describes the Time-of-Flight setup including the vacuum chamber and Langmuir probe.

3.1 Thin Film Fabrication

To explore the influence of the grain size of the thin Au films on nanoparticle generation, it was important to produce a set of samples with a range of grain microstructures. For this reason, two successful applications for funding were made; the first through the National Access Programme (NAP) in Tyndall, University College Cork, Ireland and the second through a European Access
Programme in Phillips, Eindhoven (EUMINAfab). Both programmes provided access to equipment for thin film fabrication, at no cost to the end user. The NAP programme facilitated the fabrication of Au films of different thicknesses on different substrates (Set I). The EUMINAfab programme facilitated the fabrication of 20 nm thick Au films at a combination of different deposition temperatures and rates (Set II).

The Set I films allowed the investigation the impact of different film thicknesses and substrates on the grain microstructure and laser-material interactions. The Set II films facilitated the investigation into the influence of the grain microstructure on the laser-material interactions and nanoparticle production.

3.1.1 Set I Au Films

The Set I Au films were fabricated through funding secured with the National Access Programme (NAP). NAP is funded by Science Foundation Ireland, with a view to providing access for researchers based across Ireland to the state-of-the-art research facilities and equipment located at Tyndall National Institute at University College Cork. Funding was secured for the fabrication of Au films of six different thicknesses deposited onto three different substrates.

Thin Au films of 10, 15, 20, 25, 30 and 90 nm thicknesses were deposited via e-beam evaporation onto three different substrates, Sapphire, Quartz and Silicon. The substrates were selected based on their common usage in thin film applications, differing, yet simple, crystal structures and relative ease of their dicing. The substrates also provided a range of optical, thermal and physical properties. Some of the physical properties of these substrates are listed in Table 3.
Table 3: Summary of physical properties of the three substrates used for Au film fabrication.

<table>
<thead>
<tr>
<th>Property</th>
<th>Silicon (Si)</th>
<th>Single crystalline Quartz</th>
<th>Sapphire (Al₂O₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>µm</td>
<td>525</td>
<td>500</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Diamond Cubic</td>
<td>α-trigonal β-hexagonal</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Unit cell</td>
<td>Å</td>
<td>a=5.4307</td>
<td>a=4.9133 c=5.4053</td>
</tr>
<tr>
<td>Density</td>
<td>g cm⁻³ (293K)</td>
<td>2.33</td>
<td>2.62</td>
</tr>
<tr>
<td>Melting Point</td>
<td>K</td>
<td>1683</td>
<td>1943</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>W m⁻¹ K⁻¹ (300K)</td>
<td>149</td>
<td>3</td>
</tr>
<tr>
<td>Work Function</td>
<td>eV</td>
<td>4.52</td>
<td>1.2</td>
</tr>
<tr>
<td>Band Gap</td>
<td>eV</td>
<td>1.12</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Since the silicon substrate was exposed to air prior to Au deposition, there was a high likelihood that a thin amorphous oxide layer (SiO₂) would form on its surface. The thickness of the oxide layer that forms on a silicon substrate under clean room conditions was determined as 6.7 Å [109]. Therefore, when considering the deposition of an Au film onto the substrate, the interaction would be with the oxide layer. For this reason, the silicon substrate is termed Silica throughout this thesis.

Fabrication Method

The first stage was to dice each of the substrates into sample pieces, prior to Au film deposition. Wafers of each of the three substrates were affixed to a thin flexible polymer and placed in the High Precision Wafer Dicer (Disco HiTec 3350). Each wafer was diced into chips of 0.9 cm² x 0.9 cm² squares. Dicing of the Sapphire substrate resulted in the use of large volumes of de-ionised water to cool the blade due to the relatively long period required to dice.

The diced wafers were then cleaned using a jet of de-ionised water to remove any debris. The diced wafers were passed to the Central Fabrication Facility with the e-beam evaporator (Temescal FC 2000) operated in a clean room (Class 10,000). The e-beam evaporator operated at a pressure of 6x10⁻⁷ Torr and was fitted with an aluminium shadow mask that was fabricated to block the deposition of Au onto a 1 mm border of each diced square. This border would
facilitate measurements of the film thickness, by providing an area with a step from the substrate surface to the film surface that could be measured using AFM. A test Silicon wafer was always placed into the system alongside the substrates during deposition, so that the film thickness could be verified using a profilometer at the time of fabrication.

Typically, an adhesion layer is deposited onto the substrate to improve the poor adhesion strength of an Au film to the substrate, yet this would complicate the study. As an alternative, an ion etch of the substrate surface was carried out for 20 seconds prior to Au deposition. To achieve the ion etch of the surface, Argon gas was circulated around the chamber for several minutes, before the tungsten filament was switched on causing ionisation of the gas and producing an Argon Ion (Ar⁺) beam that plasma etches the substrate surface.

An electron beam was subsequently focused into the crucible containing a piece of Au (~150g) and circulated around its surface. The power of the beam was set firstly to 8.5-9% of the full power (4 kW), in order to melt the Au, before it was ramped up to 16%, which resulted in Au evaporation. The deposition rate was set to 3 nm / min with an error of ± 1 nm / min. The chamber temperature was preset to 25°C, but varied from 25-36.1°C during film deposition.

3.1.2 Set II Au Films

The Set II Au films were fabricated through the EUMINAFab funding scheme. The EUMINAFab programme is a European wide scheme that began in 2009 and is funded by the European Commission under the FP7 Capacities programme. The programme provides free access to equipment and expertise at over 37 locations across Europe.

The MiPlaza Phillips Research Europe group in the Netherlands was targeted, as it provided the sputtering equipment and expertise to achieve the fabrication of thin Au films at different deposition temperatures and rates. Sputtering is a versatile technique for controlling the film properties, such as film uniformity and grain microstructure. Control of the deposition parameters enabled the
selective control of the grain microstructures. It should be noted that the fabrication of such films was not possible through the NAP programme.

The decision of which deposition rates and temperatures to apply to achieve a range of grain microstructures required a testing period. A number of 20 nm films were produced at extreme deposition rates and temperatures in MiPlaza and sent to NUI Galway for AFM analysis. The topography of the films was measured from AFM images, from which a combination of deposition rates and deposition temperatures were selected to produce a range of grain microstructures. Au films of 20 nm thickness were deposited onto Quartz substrates via the sputtering technique with one of five combinations of different deposition rates and temperatures. The deposition temperatures selected were 20, 200 and 450°C (at 15 nm / min) and the deposition rates were 5, 15 and 30 nm / min (at 20°C). The fabrication of these films enabled the study into the influence of deposition parameters on the Au film growth and grain microstructures, which would potentially impact on the laser-material interaction and the nanoparticle formation.

Fabrication Method

The quartz substrate was first diced through 50% of its thickness into 1 mm² squares prior to Au deposition. This meant that all of the pieces of substrate remained intact during Au film deposition but could later be broken off when required. The substrate was then mounted inside the sputtering system (Veeco Nexus Ion Beam deposition system). The settings for substrate temperature and deposition rate were then selected. A vacuum is generated inside the vacuum chamber and a bulk Au target is bombarded with positively charged argon ions (Ar⁺), which results in the formation of a plasma. The bombardment of ions onto the Au target does not heat the Au to high enough temperatures to vaporise the material, but the high kinetic energy of the Ar⁺ ions is transferred to the Au target. The transferred energy exceeds the binding energy of an Au atom and causes neutral atoms to be ejected via momentum transfer in a process called sputtering. These sputtered atoms of Au then deposit onto the Quartz substrate, which is located at the cathode. The number of atoms that are ejected depends on
the incident angle of the ion, the mass of both the ion and the target atoms and
the binding energy of the target material atoms.

3.2 Physical Properties of Thin Films

The sets of Au films described in Section 3.1 were characterized using a range of
techniques described in this section.

3.2.1 Atomic Force Microscopy

An Atomic Force Microscope (AFM) was used to measure such physical
properties as the film thickness, grain microstructure and surface roughness.

AFM functions using an oscillating cantilever with a sharp tip or probe at its end
that can either come in constant contact with the sample surface (contact mode)
or ‘tap’ the surface (tapping mode). The inter-atomic forces between the probe
and the sample will cause mechanical deflections of the cantilever. The
displacement of the cantilever is measured by reflecting laser light off the back
of the cantilever and onto a photodiode. The photodetector then produces various
images based on the deflections, twisting and other movements of the cantilever
as it moves across the sample surface.

The AFM (Agilent 5500) was operated in contact mode using a cantilever
(Nanosensors™ PPP-Contr, resonance frequency 13 kHz, force constant ~ 0.2
N/m) with a Silicon Nitride tip (< 7 nm tip radius). The topographical images
were collected at approximately 2 lines / s, with feedback gains in the range of 1-
5%. The resolution for each image was 256 pixels / line, which equates to 4 nm
per pixel resolution per 1 µm line. The exact settings were varied for each film to
optimise the quality of the image.
3.2.2 Film Thickness

All Au films were fabricated with the desired nominal thicknesses of 10, 15, 20, 25, 30 and 90 nm. The control of the film thickness is more difficult with e-beam evaporation than for sputtering and therefore it was important to verify the deposited film thickness after fabrication. The thicknesses of the Set I films, fabricated via e-beam evaporation, were measured at the time of fabrication using an interferometer and verified later with AFM analysis. Due to fabrication restrictions, the thin Au films were deposited simultaneously on Sapphire and Quartz, but were deposited on a separate occasion on the Silica substrate. The mean film thickness of five measurements made with the interferometer of the Set I films are displayed in Table 4. The standard deviation of these measurements was 1.4 nm.

Table 4: Measured film thickness of Au films on different substrates relative to their nominal thickness.

<table>
<thead>
<tr>
<th>Nominal Au Film Thickness / nm</th>
<th>Substrates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sapphire</td>
</tr>
<tr>
<td>10</td>
<td>7.2</td>
</tr>
<tr>
<td>15</td>
<td>17.3</td>
</tr>
<tr>
<td>20</td>
<td>21.4</td>
</tr>
<tr>
<td>25</td>
<td>24.3</td>
</tr>
<tr>
<td>30</td>
<td>32.5</td>
</tr>
<tr>
<td>90</td>
<td>91.0</td>
</tr>
</tbody>
</table>

An error in the exact film thickness achievable is inherent to the system used for fabrication, but, on average, the actual thickness varied just 2.5% from the nominal film thickness. Measurements of film thickness made with an interferometer are quick, but they can also result in some error, due to the high transmittance of the thin Au films. In order to verify these measurements, six films of varying thicknesses were selected and measured using AFM. All Set I films were fabricated with a 1 mm border to allow for the step height AFM measurement. A topographical AFM image was collected across a 100 x 100 µm area at the edge of the film. The image included a large area of both the substrate
surface and the Au film surface. The average heights across the substrate surface and the film surface were then calculated and the film thickness was determined as the difference between them. An example image of a step from the surface of the Quartz substrate to the surface of a 90 nm thick Au film is shown in Figure 10.

![Image of the step height of a 90 nm thick Au film on Quartz, as observed using AFM.](image)

**Figure 10:** Image of the step height of a 90 nm thick Au film on Quartz, as observed using AFM.

All AFM measurements were in good agreement with the interferometry readings and therefore the thicknesses of the films will be referred to by their nominal thickness throughout this thesis.

### 3.2.3 Grain Microstructure

Topography images were collected over 4, 1 and 0.25 µm² areas. The following steps were implemented using ImageJ software to analyse the grain microstructure of each image:

1. Set the scale-bar of the image (pixels to nm)
2. Crop image to remove scale bar.
3. Enhance Contrast / Remove noise
4. Select ‘Find edges’ to identify grain boundaries
5. Make the image binary ((black and white only)
6. Select Watershed Segmentation Algorithm
7. Select Voronoi Algorithm
8. Select ‘Analyse Particles’
Two algorithms were applied during the analysis of the grain size; Watershed and Voronoi. These algorithms were applied to each image to help distinguish the positions of the grain boundaries.

The Watershed algorithm is used to distinguish between particles that are in contact with one another. Once a binary image has been created the image contains black grains on a white background. The algorithm distinguishes where the grain boundaries are located by detecting the ultimate eroded points (UEPs) and enhances them until the edge of the particle is evident. An example of how the watershed algorithm works is illustrated below.

Following the Watershed algorithm, the boundaries of the grains can include additional lines that affect measurements, i.e. where UEPs are enhanced multiple times to complicate the grain boundaries. An example of how the Voronoi algorithm was used on an Au film to distinguish the grain boundaries is shown in Figure 12.

Figure 11: Image taken from ImageJ User Guide [110]. Images illustrate how the Watershed segmentation algorithm can distinguish grain boundaries.

Figure 12: (a) AFM image of grains (b) Following the Watershed segmentation algorithm (c) Following the Voronoi algorithm
The grain size was then determined using ‘Analyse Particles’, which scans the image and detects the grain boundaries. As the grains are largely spherical, the diameter of each grain is determined from the measured spherical area.

Topographical images were also acquired of the substrates, Sapphire, Quartz and Silica. The interaction between the tip and the substrate differs from the interaction with the Au surface and therefore different parameters were applied. The substrates were imaged at 1 line / second over a 1 µm² area. The deflection range was reduced and the feedback gains were raised to 5%. For each Au film property, over 500 grains were imaged and analysed from at least three different film samples.

3.2.4 Film Roughness

AFM was also used to determine the surface roughness of the Au films and substrates. Typically, the arithmetical mean height, Sa, has been used as an indicator of the mean surface roughness, but is now deprecated and is replaced with the root mean square height, Sq as per the ISO 25178-2 standard (EUR 15178N). Sq gives the standard deviation of the height distribution for a given area, A, otherwise known as the root mean square (RMS) surface roughness. The standard deviation for the amplitudes of the surface is determined (RMS) using the following equation.

\[
S_q = \sqrt{\frac{1}{A} \int_A \int_A z^2(x,y) \, dx \, dy}
\]

Equation 22

Topography images were collected of 1 x 1 µm areas of each sample and the surface roughness, Sq was averaged over six different images.

3.2.5 Film Adhesion

All the films were fabricated without an adhesion layer that is typically a thin
deposit of titanium that aids the adhesion between an Au film and substrate. The presence of an adhesion layer would have further complicated the understanding of the laser-material interactions and the composition of nanoparticles that formed during laser ablation.

The adhesion of the films to the substrate was tested qualitatively using the Peel-Test set out in ASTM standardized Practice for Qualitative Adhesion Testing of Metallic Coatings [111]. 3M-610 Scotch Tape was placed over the thin film surface and pulled away at 90° to the thin film surface in a smooth movement. The rate of pull was standardized as best as possible and the applied tape dimensions was also standardized.

The adhesion test is qualitative but also a good indicator of the strength of adhesion between the film and the substrate. If the film remains perfectly adhered to the substrate following the test, this indicates that the bonding between the film and substrate is greater than the cohesive strength of either. ASTM defines adhesion as the ‘condition in which two surfaces are held together by either valence forces or by mechanical anchoring or by both together’ [111]. The three factors affecting adhesion are:

1) The bonding at the film-substrate interface
2) The amount and distribution of intrinsic stress at the interface
3) The mechanism for fracture that will result in failure of adhesion.

### 3.3 Optical Properties of Thin Films

To assess the influence of different factors on the laser-material interaction, the optical properties of the material must first be investigated. The complex material response to an incident laser was discussed earlier in Section 2.2.1. Incident laser light on a material can be reflected, absorbed or transmitted at the air-film interface. The absorbed portion of laser light can be ascertained by subtracting the transmitted and reflected portions from the applied laser fluence. In this section, the method for measuring the reflectance and transmittance of and
through the Au thin films are presented.

3.3.1 Integrating Sphere

Reflectivity measurements were made using a light source, an integrating sphere and a wavelength appropriate photodetector. The integrating sphere was a 100 mm, hollow sphere with a highly reflective BaSO$_4$ coating inside and three access ports. The port at the top of the sphere allows laser light to enter the sphere and the port at the bottom accommodates the sample holder, on which a sample is mounted at an 8° angle. The angle of the sample is imperative to ensure that the specularly reflected light does not travel back again through the entrance port at the top of the sphere. The port on the side of the sphere accommodates a photodiode, which detects the diffusely scattered light around the integrating sphere. The photodiode is protected by a baffle to ensure that the light has been integrated around the sphere before being incident on the photodetector. A photo of the integrating sphere setup is shown in Figure 13.

Figure 13: Photograph of the Integrating Sphere in position for reflectance measurements. The Integrating sphere (1) is orientated using a rotary stage (2). The laser beam (Green line) is directed by a series of mirrors into the galvanometer (3) and onto the sample on the sample holder (4) at the base of the integrating sphere. The rotary stage is mounted on an Aerotech stage (5) for XYZ alignment and a camera (6) is used to aid alignment. Note: the photodetector is located on the back of the integrating sphere and is not visible in this photograph.
The sample holder had a hole in the base (50 mm in diameter) so that any laser light that transmitted through the samples was not reflected from the sample holder back into the sphere. Therefore before a sample was placed on the holder, the laser was aligned through the entrance port at the top of the sphere and through this hole in the sample holder at the base of the integrating sphere.

When light is incident on a sample, the light is partially reflected and is diffusely scattered by the walls until the intensity of light inside the sphere reaches a steady state level at all points inside the sphere. A steady-state is reached within a few nanoseconds of the light being reflected [112]. The total reflected radiation is collected and integrated by the sphere and a signal is delivered to the baffled detector. As long as the steady-state regime has been reached, the exchange of radiation between two areas on the sphere is independent of the viewing angle and the distance between the two areas. This therefore means that the fraction of flux at any point in the sphere is the same as at any other point.

The percentage of the incident light hitting the detector port is typically between 2-10% and depends on the sphere surface area and the fraction for the detector port. There is also an absorbance by the sphere walls that is typically in the range of 1.1-1.7 %. Items located inside the sphere, including baffles and ports also absorb some of the energy of the radiant source and decrease the spatial uniformity of the sphere.

The method of achieving reliable reflectivity results using an integrating sphere is discussed in depth in the literature. One method is to measure the reflectance of a reference sample and then replace it with the sample. However, by replacing the high reflectivity reference sample with a low reflectivity sample each time will result in a substitution error, whereby samples appear less reflecting than they are [112]. Double beams have been discussed as a better alternative, in which the sample is mounted in the standard way and a reference beam enters the sphere through a second entry port and reflects off the sphere wall. This method avoids such a substitution error. However, given restrictions in terms of available equipment, a single beam method by Hanssen was selected, which minimises substitution errors [113]. This method places both the reference sample and the
target sample adjacent to one another in the sphere, and the sphere is rotated to measure the reflectivity from each.

3.3.2 Reflectance Measurements

The integrating sphere was mounted on a rotary stage and the barium sulphate (BaSO₄) reference sample was placed on the sample holder adjacent to the sample. The laser light was focused onto the target surface using a computer-operated Scanlab Galvanometer and a telecentric f-theta lens \( f = 100 \text{mm} \). The integrating sphere was rotated one way to determine the reflectance from the reference sample and then tilted back to determine the reflectance of the sample. The reflected portion of light was detected by photodetectors, which generated a current that was read on the oscilloscope.

Photodetectors

Since the ablation threshold fluence of the thin Au films was very low, the applied fluence for reflectance measurements had to be even lower. This posed a problem of detecting the reflected light, since only a portion of the incident light was reflected and then integrated around the entire surface area of the sphere (31416 mm²) and the photodetector typically occupies only 1 mm² of the surface. This meant that, of the laser light that is reflected from the target, approximately 0.0025% is incident on the photodetector. Consequently, highly sensitive photodetectors were sourced at each wavelength to enable detection of very low photon densities. The photodiode responsivity (A/W) is the ratio of radiant energy (W cm⁻²) incident on the photodiode to the photocurrent output (A cm⁻²).

The first photodetector used for UV and Green reflectance measurements was a Thorlabs PDA25K – GaP Switchable Gain detector (150-550 nm). The detector provided a relatively large detection area (4.8 mm²) and a variable gain (0-70 dB) that enabled amplification of the induced current. The photodetector therefore made up 0.015% of the sphere surface and therefore was able to capture a larger portion of reflected light.
The second photodetector used for the IR reflectance measurements was a Thorlabs PDA50B photodetector (800-1800 nm). The detector had a relatively large detection area (19.6 mm²) that therefore occupied 0.06% of the sphere surface and was able to capture a larger portion of the reflected light. The photodetector also had a variable gain (0-70 dB) that allowed for greater amplification of the generated current.

**Oscilloscope**

The photodetectors were connected to a digital phosphor oscilloscope (Tektronix TDS 5054B) via a 50 Ω resistor. The reflected light from the samples was incident on the photodetector thereby generating a current that was interpreted as a voltage – time waveform on the oscilloscope. To acquire accurate data for a single shot event, the setting of Real-Time Sampling was used, which digitizes all of the points it acquires using one trigger event.

The voltage generated was not always sufficient to trigger the oscilloscope and instead the falling edge of the square pulse (2.5 V) from the Pulse Picker was used. The falling edge of the Pulse Picker pulse triggers the release of the femtosecond laser pulse, which arrives at the integrating sphere 48 ns later.

**Reflectivity - Reference**

The reference sample used in this study was Barium Sulphate (BaSO₄), which is the same base for the reflective coating on the inside of the sphere. The BaSO₄ powder was compacted into a holder and mounted adjacent to the film sample on the sample holder, which attached to the base of the integrating sphere. However, as with most samples, the reflectivity of BaSO₄ is not 100% across all wavelengths. Therefore for the three wavelengths used, 343 nm, 515 nm and 1030 nm in this study, the measured reflectivity of BaSO₄ was taken as 97%, 98% and 98% respectively, from which a 100% value was determined [114].

**Reflectivity - Samples**

A single laser pulse was applied to each sample at a sufficiently low fluence (40 mJ cm⁻²) that did not result in any damage to the Au films. The reflectivity of samples was deduced from the voltage-time waveforms on the oscilloscope.
Since the photodetectors produced characteristic rise and fall times, the reflectance values were interpreted from the peak voltage generated for the sample and was compared to the peak voltage generated for the Barium Sulphate reference to generate a percentage reflectance.

The shape of the waveform was characteristic of the photodiode rather than the detected light (i.e. fixed rise and fall time) and therefore only the peak voltage varied depending on the photons incident on the photodetector. This was verified as the detected peak voltage increased linearly with the laser pulse energy as shown in Figure 14a. It was also important to verify that the reflectance of the films did not vary with laser pulse energy. The reflectance of a 20 nm thick Au film on Quartz is shown to be constant regardless of laser pulse energy in Figure 14b. The variation in the reflectance values at different pulse energies was measured as 1.6%.

![Figure 14: (a) Linear relationship between the laser pulse energy and the peak voltage and (b) Reflectance of 20 nm thick Au film on Quartz independent of the laser pulse energy](image)

3.3.3 Transmittance Calculations

Ideally, the transmittance through the Au films would also be measured using the integrating sphere, with the film placed on top of the sphere and the transmitted light measured using the same method as described in Section 3.3.2. However, the substrate, on which the Au film was deposited, prevents such measurements. Consequently, the transmittance through the Au films was instead calculated using Kidger optical software, which accounts for variation in optical properties due to film thickness and also contributions from interference between multiple
layers of a stack. The software requires the input of the real and imaginary parts of the refractive index, \( n \) and \( k \), respectively of the film and substrate and also the thickness of each layer. Values for \( n \) and \( k \) were taken from Palik [36]. From these values, the transmittance through the Au films were predicted as described by Lewis [115]. This software was also used to verify the reflectance values measured using the integrating sphere.

### 3.4 Femtosecond Laser System

All of the experiments were carried out in an ISO Class 7 clean room. The ISO requirements list that the number of particles greater than 0.5 \( \mu m \) in size must be limited to 352,000 \( m^{-3} \) and the number of particles greater than 5 \( \mu m \) in size is limited to 2930 \( m^{-3} \). The equipment is set on optical tables that minimise vibrations.

The femtosecond (fs) laser (Amplitude Systemes s-Pulse HP) used in this study was a diode-pumped ultra-fast solid-state laser with a Ytterbium-doped laser medium. The system comprised of a laser head and a bespoke interface box and were shown in Figure 1 and Figure 3, respectively. The laser head contains a femtosecond oscillator, regenerative amplifier and a pulse-picker and the interface box enables harmonic generation, pulse compression to 50 \( fs \) and power attenuation. The theory of ultra-short laser pulse generation and amplification, harmonic generation and pulse picking were discussed in Section 2.1.

### 3.4.1 Laser Electrical Signals

The amplification and pulse picking of laser pulses is triggered by the electrical signals generated by the laser power supply. A comprehensive understanding of the laser electrical signals was also necessary for the setup of the plasma monitoring and plume imaging that is described later in this chapter.
The laser electrical signals were monitored by connecting BNC cables to the BNC outputs of the laser head to an oscilloscope. Low power oscillator pulses are generated every 20 ns and are shown in Figure 15a. The amplification of these oscillator pulses is dictated by the repetition rate specified in the software. The Amplifier pulse (Yellow) is a 2.5V square pulse and is shown in Figure 15b. During this pulse, an oscillator pulse is amplified (Blue). The falling edge of the Amplifier pulse (Yellow) triggers the release of a femtosecond laser pulse.

The Pulse Picker is typically used to achieve a more stable energy output of laser pulses. The repetition rate of the Pulse Picker must be equal to or less than the Amplifier repetition rate. The rising edge of the Amplifier pulse (Yellow) triggers the Pulse Picker 2.5V pulse (Pink) following a delay. The Pulse Picker (PP) pulse always lasts 1000 ns and the delay varies accordingly. The falling edges of both Amplifier and Pulse Picker TTL pulses always occurs at the same time but may differ in frequency according to the set repetition rates. If the PP is utilised, it is the falling edge of the PP pulse that triggers the release of the femtosecond laser pulse.

![Figure 15: Voltage – Time plots extracted from oscilloscope of the (a) Femtosecond oscillator pulses generated every 20ns and (b) the Amplifier pulse triggering the amplification of the oscillator pulses and the pulse picker pulse that is triggered by the rising edge of the amplifier pulse following a delay of 160 ns.](image-url)
3.4.2 Laser Triggering and Timing

The setups for plasma emission and plume imaging required two factors. The first requirement was the generation of a single femtosecond laser pulse. The second requirement was the measurement of the arrival time of the femtosecond laser at the stage.

**Single Pulse Generation**

It was not possible to generate single laser pulses using the laser software. Therefore an external pulse generator was used to trigger the PP pulse to release a single laser pulse. A cable connected the DDG to the Trigger BNC connection of the laser head. A square pulse with a rising edge in excess of 2V was required to trigger the PP. A 5V TTL pulse of 1 µs duration was used to trigger the PP using the Single Shot mode. The PP pulse lasts for 1000 ns and the falling edge triggered the release of a single femtosecond laser pulse.

The BNC connection that monitors the PP (Monitor Ext) was connected to the oscilloscope, which meant the falling edge of the PP pulse would trigger data collection by the oscilloscope. The oscilloscope was set up with the window triggering system, whereby the oscilloscope is initially triggered when a pulse in excess of 2V arrives, but the Trigger time relates to when this pulse falls below 0.8V.

Since a pulse generator was being used to pick single laser pulses for ablation, it was imperative that the laser energies of the laser pulses were stable. The energy of the pulses was dependent on the duration of the storage time between two amplification cycles and therefore the pulse energies were more unstable at higher repetition rates. The repetition rate was used to attain lower laser energies, so a balance was achieved for these experiments by selecting an amplifier and PP repetition rate of 5 kHz. The pulse-to-pulse stability was determined an average of 25 consecutive laser pulses, which produced a standard deviation of 2.7%.
Time of arrival of femtosecond laser pulse

In order to ascertain the TOF of the plasma emission, the arrival time of the femtosecond laser at the target material, $t_0$, was required. As stated in the previous section, data collection by the oscilloscope was triggered by the falling edge of the PP pulse, which also triggered the release of the femtosecond laser pulse. The time for the laser pulse to then arrive at the target material, $t_0$, was required, as all TOF measurements would be made relative to that time.

The time of arrival of the femtosecond laser pulse, $t_0$, was determined using a wavelength-appropriate photodiode at the vacuum chamber stage. The same photodetector (PDA25K) was used at UV and Green laser wavelengths while a different photodetector was used for IR wavelength (PDA50B).

The time between the falling edge of the Pulse Picker pulse (Trigger) and the detection of the laser pulse ($t = 0$) is shown for UV and IR wavelengths in Figure 16a and b, respectively.

![Figure 16](image)

**Figure 16**: Images of the oscilloscope data of the falling edge (Trigger) of the pulse picker pulse (PP) and the onset of the photodiode pulse (PD) which represents the arrival of the femtosecond laser pulse ($t = 0$). The data is shown for laser pulses at (a) UV wavelength and (b) IR wavelength.

The time of the arrival of the femtosecond laser pulse, $t_0$, was determined from the onset of the photodiode voltage relative to the triggering falling edge of the pulse picker pulse. This data was presented for UV and IR wavelengths in Figure 16a and b, respectively. For UV and Green laser pulses, $t_0$ was determined as 98 ns and 96 ns following the triggering falling edge of the pulse picker pulse. The difference in time is due to the shorter pathway through the interface box for
Green than UV wavelength. The detection of the time of arrival, \( t_0 \), for IR pulses was more complex due to the apparent leakage of laser light from the system during amplification. This was not observed at UV and Green wavelengths, due to the longer pathway through the harmonic crystals. The \( t_0 \) at IR wavelength was deduced as 72 ns.

3.4.3 Standard Laser Parameters

The standard working parameters of the laser output are shown in Table 5. Many of the laser parameters are variable and this Section details the method for measuring them.

<table>
<thead>
<tr>
<th>Laser Parameter</th>
<th>Symbol</th>
<th>Range</th>
</tr>
</thead>
</table>
| Laser Wavelengths     | \( \lambda \) | 1030 nm (fundamental)  
515 nm (2\(^{nd}\) harmonic - 50\% conversion)  
343 nm (3\(^{rd}\) harmonic - 30\% conversion) |
| Power                 | \( P \) | 0.04 mW - 4 W                                                          |
| Pulse Energy          | \( E_p \) | 40 \( \mu \)J - 1 mJ                                                  |
| Pulse Duration        | \( \tau_p \) | 50 fs - 3 ps                                                          |
| Repetition Rate       | \( Q \) | 1 Hz - 300 kHz                                                        |
| M\(^2\) Beam Quality  |        | 1.2                                                                   |
| Beam Shape            |        | TEM\(_{\infty}\), Gaussian                                          |

Laser Pulse Duration

The pulse duration of the laser is measured using the APE auto-correlator. The auto-correlator operated for IR wavelengths only and therefore the pulse duration was inferred from this value for the other laser wavelengths used. The auto-correlator was set to the most sensitive setting with a high gain value. The laser was then directed into the inlet of the auto-correlator with the aid of an IR viewer. Two mirrors were then used to optimize the precision with which the laser entered the auto-correlator, using the signal that was produced on the auto-
correlator screen for guidance. Once this coarse adjustment was completed, the fine adjustment was carried out by further mirror adjustments and the lowering of both the gain and sensitivity until the maximum signal was produced on the auto-correlator screen. The offset must also be carefully monitored throughout, as it often falls below zero and distorts the temporal beam shape. The pulse duration is then calculated from the full width half maximum (FWHM) of the pulse shape produced. A fit is produced called sech2 (favoured over a Gaussian fit as it matches better). The measured value for the pulse duration here was 520 fs. The longest pulse length achievable with this system is approximately 3.2ps and the shortest was 300 fs. The system does have capabilities to reach pulses of 50 fs but this falls outside of the scope of this study. The details of these measurements can then be processed on the computer software via the R532 cable.

**Laser Power**

The output laser power could be varied in two ways. The first used the auto-correlator that controlled the direction of the amplified laser beam using a waveplate. By altering the waveplate, the laser power was directed to either the IR output of the interface box or through to the second and third harmonic crystals.

If UV or Green laser wavelengths are required, their output powers can be adjusted by manipulating the harmonic crystal orientation. For example, to maximize the laser output of the Green wavelength, the horizontal alignment can be adjusted on the SHG crystal to maximize the IR to Green photon conversion and the vertical alignment on the THG crystal to minimize the IR and Green to UV photon conversion. To monitor the power during these adjustments a power meter (Ophir) was used with one of two thermal heads depending on the power range.
Laser Pulse Energy

The laser pulse energy, \( E_p \) was then determined by combining the measured laser power, \( \overline{P} \), with the repetition rate, \( Q \), using the equation:

\[
E_p = \frac{\overline{P}}{Q}
\]

Equation 23

Laser Intensity Profile

The Gaussian profile refers to the propagation integral that describes the propagation of the electromagnetic field associated with a laser beam in a cavity. Solutions of these propagation integrals occur when the wave propagates as a standing wave, such that the transverse field is the same in both amplitude and phase after each length of the cavity. These solutions are Eigenmodes and are termed electromagnetic modes (TEM) and describe the intensity distribution of the laser beam. The femtosecond laser in this study operates in a TEM\(_{00}\) mode, where the subscript numbers refer to the number of nodes in the x and y directions, respectively. In the TEM\(_{00}\) mode the irradiance distribution across the beam is termed Gaussian [116]. The intensity profile of the Gaussian beam is described by

\[
I(r) = I_0 e^{-\frac{2r^2}{\omega_0^2}}
\]

Equation 24

where \( I(r) \) is the intensity at distance \( r \) from the centre, \( I_0 \) is the peak intensity and \( \omega_0 \) is the radius, at which the laser intensity falls by \( 1/e^2 \) of the peak value. As the Gaussian beam propagates in free space, at a distance \( z \), the beam converges to its narrowest value of \( \omega_0 \) along the beam axis and is called the beam waist, \( w \), which is defined by

\[
w = \omega_0 \sqrt{1 + \left( \frac{\lambda z}{\pi \omega_0^2} \right)^2}
\]

Equation 25
The total laser power is determined by integrating under the intensity spatial laser profile.

$$P(t) = 2\pi \int_0^\infty I(r,t) r \, dr = \frac{\pi w^2 I_0(t)}{2} \quad \text{Equation 26}$$

The beam radius for the Gaussian intensity profile, \(\omega_0\), was determined as the radius where the intensity is equal to \(1/e^2\) at the peak. The unfocussed beam diameter was measured using a Beam Profiler (Beamstar) with attenuators to reduce the laser intensity to approximately 1 W/cm². An example of the beam profile imaged is shown in Figure 17. The \(1/e^2\) diameters, \(2\omega_0\), for unfocussed laser beams of UV, Green and IR wavelengths were measured as 2.945, 2.843 and 2.657 mm, respectively.

![Example of beam profile taken of the Green laser beam](image)

**Figure 17**: Example of beam profile taken of the Green laser beam

### 3.4.4 Laser Ablation

Laser ablation is the ejection of material following the absorption of laser energy as was presented earlier in Section 2.3. To compare the laser ablation of materials, the laser fluence is a useful parameter to describe the laser energy delivered per unit area. By measuring the diameters of ablated craters at different fluences, it is also possible to determine the laser ablation threshold fluence of the material.
Laser Beam Radius, $\omega_0$

The laser fluence, $\phi$, is typically favoured over intensity, energy or power, as it eliminates the time factor from equations. The relationship between the fluence and the laser beam area is described by

$$\phi = \frac{2E_p}{\pi \omega_0^2}$$

Equation 27

The laser beam diameter, $\omega_0$, can be calculated from the gradient of the trendline through a logarithm of the laser pulse energy, $E_p$, against the squared value for the average crater diameter, $D^2$ [117].

$$D^2 = -2\omega_0^2 \ln\left(\frac{\pi \omega_0^2 \Delta H_v \delta}{2\alpha}\right) + 2\omega_0^2 \ln E_p$$

Equation 28

where $\alpha$ is the optical absorptivity, $\Delta H_v$ is the total heat required to vaporise a unit of material and $\delta$ is the film thickness.

Lines (2 mm) were laser ablated at different laser pulse energies at a mark speed of 2000 mm s$^{-1}$, so as to achieve resolved ablated craters. An optical microscope (Olympus) was used to image the ablated craters in the films using 10x, 20x and 50x objectives. The film was placed on a three axis manual stage and focused firstly using a coarse and then a finer focus. Images of the ablated craters were acquired using a camera attached to the microscope. The craters were measured using software called µVision, which is based on LabVIEW. The diameters of the craters are determined when three points are selected around the edge of the spherical crater and a circle is fitted to the hole. The average diameter, $D$ of ten craters per laser pulse energy was measured. A plot of $\ln E_p$ versus $D^2$ was then plotted, from which a value of $\omega_0$ was determined from the gradient which is equal to $2\omega_0^2$. 
Laser Ablation Threshold Fluence, $\phi_{th}$

The minimum average absorbed laser fluence required to initiate ablation, $\phi_{th}$, is an important parameter of the laser-material interaction. The value for $\phi_{th}$ is determined by measuring the diameter of the craters ablated for different laser fluences, $\phi_0$, and then deriving the threshold fluence from the linear relationship between $D^2$ and $\phi_0$ as shown below:

$$D^2 = 2\phi_0^2 \ln\left(\frac{\phi_0}{\phi_{th}}\right)$$

Equation 29

The square of the diameter, $D^2$, is linearly proportional to the laser fluences applied and a plot of these values can be used to determine the ablation threshold fluence, $\phi_{th}$, by extrapolating back to the intercept with the x-axis [118].

3.5 Plasma Generation

Laser ablation resulted in the ejection of electrons and ions from the thin Au films that were then detected under vacuum conditions using a Langmuir probe. A positive or negative voltage bias could be applied to the probe, so as to detect either electrons or (positive) ions, respectively. The current generated by the impinging charges was interpreted as a voltage on an oscilloscope, and this data could be analysed to give the number, energy and temperatures of the charges ejected during laser ablation.

3.5.1 Plasma Detection Setup

The setup used for plasma detection from thin Au films, comprised of a bespoke vacuum chamber, a vacuum pump, an oscilloscope and a pulse generator as shown in Figure 18.
**Vacuum Chamber**

The bespoke vacuum chamber was made from stainless steel and comprised of six exit ports, all of which were sealed with flanges or vacuum compatible windows. The ports included electrical connections for the Langmuir probe and tilt sensor, connections for the vacuum pump, two vacuum gauges and an optical window for the incident laser.

The vacuum chamber was connected to a combined rotary vane and turbo-molecular vacuum pump. The Edwards rotary vane roughing pump brings the pressure in the chamber to $10^{-4}$ Torr and when a sufficiently low pressure (approximately $10^{-3}$ Torr) is reached the Turbo molecular pump begins to operate. The pump has rotating fan blades that direct the gas particles towards the exhaust and enables vacuum pressures of $10^{-6}$ Torr to be reached inside the chamber. The pressure inside the chamber is measured using two pressure gauges. The Pirani gauge measures the pressure down to $10^{-4}$ Torr and the ionizing pressure gauge can measure from $10^{-3}$ to $10^{-6}$ Torr. All experiments were carried out in the range of $10^{-5}$ – $10^{-6}$ Torr ($0.13$-$1.13$ mPa).

Within the chamber, the thin film was placed on a vacuum compatible DC servo rotary stage (NAI MM-3M-R) that allowed the sample to be rotated in between...
each incident laser pulse to always allow for the ablation of a new piece of material each time.

**Langmuir Probe**

The Langmuir probe comprises of a tungsten wire insulated by a dielectric and then surrounded by a copper shield. The probe is exposed at the tip of the wire with a flat circular face with an area of 0.011 cm$^2$. The probe was attached to the door of the vacuum chamber and was orientated normal to the target surface at a distance of 3 cm. The orientation of the probe was monitored using a tilt sensor (Assemtech EDX90XA) and the angle was viewed through a HyperTerminal programme. Since the plasma and plume material is predominantly ejected along the normal to the target, the probe was angled at 0° from the normal so as to maximise the signal detected. The laser pulses were then focused by wavelength appropriate lenses (f = 250 mm) onto the target surface at an angle of 5° to normal. The orientation of the incident laser on the fresh sample with the Langmuir probe was maintained throughout. Diagrams of the Langmuir probe setup are illustrated in Figure 19.

![Diagram of the setup with the Langmuir probe orientated at 0° at a distance, d, above the target surface, perpendicular to the expanding plasma. The laser was incident at a 5° angle to the normal.](image)

**Figure 19:** Illustration of the setup with the Langmuir probe orientated at 0° at a distance, d, above the target surface, perpendicular to the expanding plasma. The laser was incident at a 5° angle to the normal.

A bias voltage can be applied to the Langmuir probe to distinguish between the detection of either electrons or positive ions. A bias voltage (± 30V) across the Langmuir probe was generated using a power supply via the circuit shown in Figure 20. The circuit was first described by Koopman and is therefore often referred to as the Koopman circuit [119]. When charged species impinge on the
exposed surface of the probe, a current is generated that then passes back into the circuit box and across a capacitor before detected as a voltage across a 50 Ω resistor at the oscilloscope. A high resistor (220 kΩ) prevents the current passing back to the power supply.

![Diagram of the circuits involved with creating a voltage bias across the Langmuir Probe.](image)

**Figure 20**: Diagram of the circuits involved with creating a voltage bias across the Langmuir Probe. The components within the circuit are linked with RG58 co-axial cables that have a characteristic impedance of 50 Ω and a capacitance of ~ 90 pF m⁻¹.

**Oscilloscope**

The detection of the plasma components was measured on the Textronix oscilloscope described in section 3.3.2. When charges impinged on the Langmuir probe a current was generated and a voltage was induced across a 50 Ω resistor at the oscilloscope. The waveforms were recorded as two data columns of voltage and time, which were then exported into other software for analysis. Each waveform collected consisted of 12,500 data points over a 10 µs period, equating to a temporal resolution of 0.8 ns. The typical rise and fall time of a 1 meter RG 58CU co-axial cable (R = 50 Ω and C = 90 pF m⁻¹) is 2 ns. The Langmuir probe was connected to the oscilloscope with RG 58CU co-axial BNC cables that matched the 50 Ω impedance at the oscilloscope.

Hi-res Average Acquisition mode was selected to average the voltage signal for four ablation events, each on a new piece of film. Since the current generated by the impinging charges on the probe was insufficient to consistently trigger the oscilloscope, the falling edge of the Pulse Picker pulse was used instead. Window triggering allows the oscilloscope to be triggered when an input signal rises and then falls below a threshold level (2V). A photodiode was placed on the
rotary stage and the time between the falling edge of the Pulse Picker and the arrival of the laser pulse at the stage was determined. The time of the arrival of the laser pulse at the stage is then termed $t_0$ with any voltage detected on the oscilloscope after this time due to the arrival of charges at the probe.

### 3.5.2 Signal Interpretation

The voltage time waveforms generated on the oscilloscope as a result of impinging charges on the Langmuir probe, can be interpreted to provide a wealth of information. The waveforms were analysed to determine the number, temperature, and kinetic energy of the charges arriving at the Langmuir probe. This section explains the relevant equations for interpreting the waveforms to deduce the following:

- a) Electron velocity, $v_e$
- b) Electron kinetic energy, $E_k$
- c) Total number of electrons, $N_e$

#### a) Electron velocity

The velocity of the charges arriving at the Langmuir probe can be determined from the time of flight (TOF). The TOF of charges, $t$, is determined from the arrival time of the incident laser light, $t_0$ until the arrival time of charges at the probe. The arrival of the electrons at the probe is determined from the time of the peak voltage observed on the oscilloscope. The distance between the film surface and the probe, $d$, is known, hence the velocity of these charges can be determined using

$$v_e = \frac{d}{t} \quad \text{Equation 30}$$

This same method can be applied to determine the velocity of the positive ions, $v_i$, when the Langmuir probe is negatively biased.
b) Kinetic Energy of Electrons

The velocity of the charges can then be used to establish the kinetic energy, \( E_K \), associated with the charges using

\[
E_k = \frac{1}{2} m_e v_e^2
\]

Equation 31

where \( m_e \) is the mass of an electron.

c) Total number of Electrons

The size of the cross-sectional area of the Langmuir probe influences the charge flux collected. The charge flux per pulse must therefore account for this cross-sectional area. The current generated at the probe due to the flux of ions was given earlier in Equation 17. Since the current in the circuit is all attributable to the charges impinging on the Langmuir probe, the number of charges incident can be determined by dividing the detected current by the charge of a single electron:

\[
\frac{I(t)}{e} = \frac{dN}{dt}
\]

Equation 32

where \( e \) is the electron charge and \( N \) is the number of particles.

The charge flux per pulse is deduced by dividing the total charges per unit area by the charge of a single electron, \( e \). Therefore the charge flux, \( Q \), is given by:

\[
Q = \frac{1}{Ae} \int_0^t I(t) \, dt
\]

Equation 33

As the probes signal is detected as a voltage on the oscilloscope, Equation 33 can be divided by the resistance, \( R \), (50 \( \Omega \)) and the voltage signal integrated over time to give the total number of electrons detected per pulse.
The integration of the voltage–time waveforms was carried out using Wire 3.3 software. Firstly, a Gaussian-Lorentzian mixed curve was fitted to each peak within the waveform and the area under the curve for different time periods could be measured.

3.6 Nanoparticle Generation

Nanoparticles were generated during the laser ablation of thin Au films with a single femtosecond laser pulse. Nanoparticles were generated from films of varying thicknesses and grain microstructures, before being imaged and measured.

3.6.1. Nanoparticle Collection

In the literature, various methods are utilized to collect nanoparticles during laser ablation, each of which introduces a bias on the size distribution of nanoparticles measured. In order to gain an insight into the ablation mechanism, this study investigated nanoparticle generation in ambient conditions and therefore a substrate is required for collection. The choice of orientation was either a substrate placed above the ablated surface, or to allow re-deposition of the nanoparticles onto the exposed substrate surface. Either method would inflect some bias on the size of nanoparticles collected.

The method of orientating the substrate above the surface results in an angular dependence of the nanoparticle spatial distribution deposited on the substrate. An additional factor with this method is the distortion of the nanoparticles caused by the impact of a molten droplet onto the substrate surface. Models have shown that metal nanoparticles generated during femtosecond laser ablation will still be in a liquid phase when impacting onto the collection substrate [77] and therefore
the nanoparticles will be influenced by the wetting angle of the metal on the substrate and possible coalescence with neighboring nanoparticles. This will ultimately result in measured nanoparticles that are larger than those ejected during ablation. The volume of nanoparticles collected on a substrate will also be difficult to determine as the wetting angle will disrupt the spherical nature of the nanoparticle. The choice of substrate is therefore also influential on the size of the nanoparticles measured due to the wetting angle that is generated. Also, if a substrate was selected where the nanoparticle has a very high wetting angle, the risk exists that the nanoparticle will not adhere to the surface at all, particularly due to the high speeds reached by the nanoparticles. Finally the height at which the substrate is orientated above the irradiated surface will also add to the size bias of the nanoparticles.

The method of collection selected for this study was to examine the nanoparticles that re-deposited onto the ablated substrate surface. Nanoparticles are predominantly ejected along the normal to the material during laser ablation and will begin to cool through collisions with ambient molecules. As their velocity slows, convection flow will cause the particles to re-deposit into the ablation crater of the substrate [120, 121]. As a single laser pulse was sufficient to remove the entire film within the crater, as shown in Section 5.2.3, the exposed substrate surface acted as the collection substrate. By allowing for the nanoparticles to re-deposit onto the surface, the nanoparticles have had sufficient time to re-solidify and were therefore not biased by the nanoparticle-substrate interaction. Any collection method will induce a bias on the nanoparticles measured, but this method resulted in a large range of nanoparticle sizes collected and significantly, the method of collection was the same for all Au films and laser parameters. Therefore the collection method does not significantly affect the comparison of nanoparticles within this study and the conclusions about differing ablation mechanisms at different wavelengths.
3.6.2 Scanning Electron Microscopy

Following laser ablation of the thin Au films, a Scanning Electron Microscope (SEM) was used to image the nanoparticles that had re-deposited onto the substrate surface. A SEM applies a voltage to an anode to accelerate primary electrons from a hot tungsten filament towards a target in a vacuum. The beam of electrons is then focused onto the target with an aperture and a set of condenser lenses. The condenser lenses are a number of apertures and magnetic lenses. The electron beam interacts with the sample within an interaction volume, the size of which is dependent on the accelerating voltage and the material properties. The higher the energy of the primary electrons, the greater the penetration depth into the material. The primary electrons transfer some energy to the electrons within the sample surface and results in a change in path of the backscattered electron. One or more electrons within the sample surface can gain sufficient energy to be ejected from the surface and these are named secondary electrons. At higher incident electron energies, X-rays may also be generated from the interaction volume. The electrons are detected and an image of the target surface is produced by the accompanying software.

Identifying SEM equipment that was capable of imaging nanoparticles of just 1 nm in size was demanding. Imaging was further complicated by the non-conductive nature of the substrates, onto which the nanoparticles had deposited, which typically resulted in charging and poor image quality. The charging of samples occurs when primary electrons impinge on a non-conducting surface and electrons accumulate on the surface. This accumulation of charges results in the deterioration of the image quality. Typically, the sample would be coated with a thin film of Au to aid conduction and hence imaging quality. However, this was clearly not an option as this would contaminate the sample. The solution was applying low accelerating voltages to minimise charging effects and to prevent the possibility of deposited nanoparticles being irradiated from the surface. However, with low accelerating voltages, the achievable resolution is reduced.

A SEM (Carl Zeiss) was selected due to its many refined capabilities to improve imaging of nanoparticles. The SEM was located in the Advanced Microscopy
Lab in CRANN, Trinity College Dublin and was accessed through the INSPIRE programme. The equipment facilitated very low accelerating voltages, which reduced charging issues. Additionally, the SEM had an In-Lens detector in addition to the secondary electron (SE) detector, which is located directly in the beam path and hence has the advantage of high detection efficiency at low accelerating voltages. The SE detector is located at the side wall of the chamber and detected secondary electrons and backscattered electrons. The Carl Zeiss equipment also provides a range of aperture sizes to improve resolution. A smaller aperture (10 µm) than the standard size (30 µm) enhanced the achievable resolution of the images. Additionally, it was possible to reduce the standard working distance from 7 mm to 3 mm, which helped to maximize the signal to noise ratio and resolution. The working distance is the distance from the focused sample surface to the objective lens. Shorter working distances were not possible as shadow effects begin to occur and the efficiency of the detector is reduced.

Three thin film samples were adhered to each metal stub using a carbon sticky tab. Three stubs were then placed on the stub carousel and locked in the chamber. The chamber was evacuated and the electron beam switched on before image acquisition. During imaging of the nanoparticles the electron beam was often distorted due to the inhomogeneity of the sample surface and the beam evolved to become elliptical rather than spherical. An electromagnetic correction called a stigmator restored the symmetry of the beam by adjusting mirrors in the X and Y directions. Stigmation correction was carried out for each sample, as well as optimization of brightness and contrast to maximize the image quality. Numerous images of the re-deposited nanoparticles were collected for each set of laser parameters and for each thin film and were later analysed and characterised. Over 250 nanoparticles were measured for each set of conditions from at least three different ablated craters.
3.6.3. Nanoparticle Characterisation

SEM images of nanoparticles were amassed, as detailed in the previous section. The images were then exported to the software, ImageJ, and a sequence of steps were carried out on each image to firstly distinguish the nanoparticles from the background and to then measure the spherical diameter of each nanoparticle. The sequence of steps is set out below:

1. Set scale-bar for the image (pixels to nanometers)
2. Crop Image to remove scale bar
3. Enhance contrast / remove noise
4. Apply a threshold range to distinguish particles from the background. A minimum threshold of 1 nm was set as this is the resolution of the SEM.
5. Make the image binary (Black and white only)
6. Analyse particles

An example of how the ImageJ software was used to identify nanoparticles is shown in Figure 21. Images were scanned to identify edges, from which the spherical area was evaluated. The diameter was determined from the area assuming the nanoparticles were spherical.

**Figure 21:** (a) SEM image of nanoparticles taken from the Carl Zeiss SEM and (b) processed image, from which the dimensions of the nanoparticles were measured. Images approximately 700 nm x 1000 nm.
3.7 Real-Time Visualisation

The visualisation of the expanding nanoparticle plume in real time was attempted using the schlieren imaging setup described in this section.

3.7.1 Schlieren Imaging Setup

The dual-field lens schlieren arrangement was implemented using the setup shown in Figure 22.

![Figure 22: Dual-field lens schlieren arrangement. Four lenses used: \( L_1 \) Nikon 50 mm / 1.2 for condenser lens, \( L_2 \) Nikon 50 mm / 1.7 for collimation, \( L_3 \) Nikon 105 mm / 2.8 and a telescopic lens arrangement for \( L_4 \). Schlieren images are taken of the ablation plume generated following laser ablation of thin Au films.]

A diode laser (CAVILUX smart, Cavitar) produces 690 nm laser pulses at up to 500 W with low coherence. The duration of the laser pulses range from 10 ns to 10 µs and either a repetition rate can be selected or the pulses can be triggered from an external source. The optical fibre has a NA of 0.37 and the output beam had a width of approximately 5 mm. Using an extended light source rather than a point source enables a depth of focus, since the light is illuminating an area within a cone. The diverging beam was focused using one of four lenses used in the schlieren setup.

The first lens, \( L_1 \), was a Nikon 50 mm / 1.2 condenser lens that focuses the diverging laser beam to a point. \( L_2 \) was a Nikon 50 mm / 1.7 and collimated the beam, which passed across the stage to \( L_3 \). \( L_3 \) was a Nikon 105 mm / 2.8 which focused the collimated light, before a telescopic lens arrangement, \( L_4 \) focused the
image onto the iCCD screen. The telescopic arrangement (L₄) comprised of a Mitotoyo M-Plan Apo objective (10x) connected to a Navitar ultrazoom lens with variable magnification (0.7x – 4.5x) and a standard adaptor (2x), which was mounted to the ICCD camera using a C-mount coupler. The Mitotyo objective has a focal length of 200 mm, a working distance of 20 mm and a numerical aperture of 0.42. The selection of all components of this schlieren setup is justified and discussed in Section 6.7.

A horizontally orientated 200 µm slit is placed at the first focal spot of the system and is coupled with a horizontally orientated knife-edge or a Hoffmann modulation contrast filter at the second focal spot of the system.

As the collimated light passes through the laser-material interaction zone, the parallel light is subjected to changes in the refractive index. The parallel light that is unaffected will continue and focus to a point and is blocked by the knife-edge. The parallel light that is refracted by the interaction zone will propagate through to the camera, where an image will form. The knife-edge blocks all light that is at the focal point of the lens system. For some applications, the cutoff by the knife-edge can prove too harsh and alternative combinations continue to be explored. Hoffmann modulation contrast filters, which are commonly used in microscopy, have overcome this phase issue and have been shown to intensify the contrast produced by small deviations compared to the knife edge [122]. A Hoffmann filter comprises of three areas that transmit different amounts of light; the knife-edge that transmits 0% of light, and the window that transmits 100% of light surrounds a narrow grey filter, which transmits 15% and provides sufficient background intensity for the image. Light that is deflected upwards passes through and results in a brightened image. Light that is deflected downwards is blocked by the knife-edge. The change in image brightness is dependent on the angle of deflection and the width of the slit.

The Andor Istar intensified charge coupled device (iCCD) was used to achieve imaging with very short exposure times (1.2 ns) and very low levels of illumination. The camera comprises of three key components; photocathode, microchannel plate (MCP) and the phosphor screen. When photons of light are incident on the photocathode, an electron is emitted and moves across a gap to
the MCP and then cascades down a channel in the MCP due to the high potential across it (500-1000V). This cascading electron causes the generation of secondary electrons, which effectively amplify the signal. The intensifier component can generate amplification of the input signal by up to $10^4$ by increasing the voltage gain across the MCP. The electrons then arrive at the Phosphor screen and an image is generated. Figure 23 shows the variation of signal to noise ratio with increasing MCP gain.

![Figure 23: Signal to noise ratio in response to increasing the MCP gain using the Andor iCCD camera](image)

The Andor iStar 740 iCCD has a 2048 x 512 array and was cooled to -20 °C for all measurements. The accompanying software enabled external triggering, controllable delays, exposure times and gate widths, that are discussed further in the following section.

The images produced required post-processing in ImageJ software to enhance the contrast and discern the nanoparticle plume expansion. Firstly, all images were compiled into a stack, so that each image underwent the same treatment. The most effective and consistent post-processing step was to enhance the contrast by histogram equalization. A histogram of each grey-scale image is produced to give the relative frequency of the intensity levels. The histogram equalization operator effectively equilibrates the range of the grey-scale palette, so that the contrast of the image is improved.
3.7.2 Temporal Alignment

The schlieren imaging setup has to be spatially and temporally aligned with the femtosecond laser pulse used for ablation of the target material. This was achieved by triggering the femtosecond pulse, Andor camera and Cavitar laser from a single DDG pulse generator. The rising edge of the single pulse sent by the DDG pulse generator triggered a single PP pulse. The rising edge of the PP pulse triggered both the Andor iCCD camera and the Cavitar laser. Following 1000 ns, the falling edge of the PP pulse triggers the release of the femtosecond laser pulse.

**DDG Pulse Generator**

A DDG pulse generator was used in single pulse mode to generate a single 2.5V pulse to trigger the femtosecond laser pulse picker (PP).

**Femtosecond Laser Pulse**

The time of the pulse arrival at the stage was required so that images were taken relative to this time. The time of arrival varied with laser wavelength. The time of arrival was determined using a photodiode relative to the rising edge of the PP pulse.

**Andor camera**

Following this triggering by the PP pulse, there are inherent delays associated with the Andor camera. An Ultrafast mode was selected to minimise these delays. A delay is incurred due to the length of time required for the triggering pulse to travel through the DDG and Gater electronics to the Intensifier Tube Photocathode, which takes a total of 24 ± 1 ns and 16 ±1 ns, respectively. The total insertion delay in Ultrafast mode is therefore 40 ± 2 ns. Following this delay a further delay can be implemented using the Gate Pulse Delay so that t=0 matched the time of arrival of the femtosecond laser pulse at the stage. Gate pulse width (0 – 25 s) is the length of time that the intensifier tube is switched
(gated) on. i.e. optical signal falls on the CCD sensor during this time and has a resolution of 25ps. The exposure time refers to the time in seconds during which light is allowed to fall on the CCD prior to the readout.

**Cavitar laser**

When the triggering pulse arrives at the Cavitar laser, delays and pulse durations can be selected in the software. The duration of the pulses can be varied between 10 ns and 10 µs. The Cavitar laser was typically triggered and remained on for a period of 5 µs to illuminate across the ablated area.

### 3.7.3 Spatial Alignment

The femtosecond laser pulse was focused using a wavelength appropriate lens onto the target surface, which was located on a translation stage in the centre of the collimated beam of the schlieren setup as shown in Figure 22.

**Translation stages**

The Au films were placed on an XYZ translational stage that was driven with DC servo motors, which were controlled by a T-cube servo controller unit. Each unit was then linked to Thorlabs software. After a crater was ablated, the stage was shifted by 100 µm, so that a new area was ablated each time.

**Lenses**

The femtosecond laser was focused onto the sample surface using a wavelength appropriate lens; UV (LMUUVB), Green (LMH532) and IR (LMH1060). All lenses had a working distance of 35 mm and a numerical aperture (NA) of 0.13. The plume was imaged using a telescopic lens setup attached to the Andor ICCD camera. A c-mount coupler attached a standard adapter with a magnification of 2x or 0.5x. This was followed by a Navitar ultra-zoom lens with an adjustable zoom lens (0.7 – 4.5 x), which finally attached to a Mitotoyo lens (10x). The Mitotoyo lens had a focal distance of 20 mm and a NA of 0.42.
3.8 Summary

This Chapter introduced all the equipment and techniques applied in the assimilation of results presented in the following three Chapters. Firstly, the fabrication of the Au films was discussed and the techniques used to characterise the films. The laser itself was also presented and how the optical properties of the films were measured and accounted for. The Chapter covered the methods for determining grain and nanoparticle size, so that they could be compared in Chapter 5. Finally, the equipment used for plasma detection was discussed, as well as the analytical methods for extracting key information about the plasma components.
Chapter 4
Thin Gold Film Characterisation

4.1 Introduction

To understand the material response of Au films to an incident laser pulse, it was first necessary to characterise the Au films, in terms of their physical and optical properties. The intention of this Chapter was to establish the impact of different physical properties, such as film thickness and grain microstructure, on the optical properties displayed by the films. This information is particularly significant, when comparing laser ablation of the films at different laser wavelengths.

Chapter 3 presented the fabrication process of Au films that delivered an array of thicknesses and substrates and this Chapter begins by exploring the variation of grain microstructures of Au films, given these different fabrication parameters. The effect of the grain microstructure on the laser-material interaction has been largely overlooked in the literature; however, the presence of grains affects the topography of the film surface that can result in changes to the optical properties of the film. Therefore the effect of the grain microstructure on the optical properties is also presented in this Chapter. This study also aims to clarify whether any relationship exists between the grain microstructure of Au films and the nanoparticle debris that form during laser ablation, the results of which are presented in Chapter 5.
Laser ablation of different materials at different laser wavelengths is typically compared using a single applied laser fluence [46, 58, 123, 124]. An alternative method is explored in this study to account for the wavelength dependence of the material optical properties and compare the laser ablation of materials at a single absorbed laser fluence. Later results use the results presented in this chapter to compare the processes of laser ablation, plasma, plume and nanoparticle generation during laser ablation of Au films at equal absorbed fluences and different laser wavelengths.

This chapter begins by presenting the absorptance of a range of Au films at three laser wavelengths. The calculated absorptances are then used to determine the absorbed laser fluences throughout this thesis. The laser ablation threshold fluence, \( \phi_{th} \), is a measurement commonly used throughout the literature to characterise and compare the laser ablation of materials [125, 126]. This Chapter incorporates the calculated absorptance by each film to determine the absorbed ablation threshold fluence and thereby exposes the effects of film thickness, grain microstructure and photon energy on Au film ablation.

As a reminder, the two sets of films fabricated for this study were as follows:

**Set I:** Au films with thicknesses 10, 15, 20, 25, 30 and 90 nm each deposited on Sapphire, Quartz and Silica via e-beam evaporation at 20\(^\circ\)C and 3 nm / min.

**Set II:** Au films with thickness of 20 nm deposited on Quartz via sputtering at a combination of different deposition temperatures (20, 200 and 450\(^\circ\)C) and deposition rates (5, 15, 30 nm / min).
The key objectives of this Chapter are as follows:

- Explore how the grain microstructure of thin Au films can be controlled by varying thicknesses, substrates and fabrication conditions.

- Determine the amount of incident laser light that is absorbed by thin Au films and identify the physical properties that affect the optical properties.

- Explore the consequences of discussing laser ablation of films in terms of the applied laser fluence, rather than the absorbed laser fluence.

- Determine the key physical properties of Au films that impact their absorbed ablation threshold fluence at different laser wavelengths.
4.2 Factors Affecting Grain Microstructure

The mechanism of polycrystalline film growth and grain formation was introduced in Section 2.2. The microstructure refers to the grains, which are volumes of crystal structures orientated in the same way divided by a grain boundary, at which another grain is orientated in a slightly different way. The grain microstructure can be deduced using Atomic Force Microscopy (AFM) to measure the topography of the film surface. An example of the topography of a 30 nm thick Au film on Quartz is provided in Figure 24, which illustrates the presence of the grains.

![Figure 24: Topographical AFM cross-section of a 30 nm thick Au film on Quartz, illustrating the topography variation of the surface over a 0.5 µm distance due to the grain microstructure.](image)

The grain microstructure of the film is characterised by the average grain diameter, $d_G$, using the method set out in Section 3.2.1. This section presents AFM images of the Au films and identifies the key factors influencing the grain microstructure that form.

4.2.1 Substrate

The influence of the substrate on the grain microstructure was determined by comparing topographical AFM images of Au films on the three substrates; Sapphire, Quartz and Silica. Figure 25 shows notable differences in the grain microstructure of 20 nm thick Au films deposited onto the three substrates. The
accompanying histograms show the distribution of the measured grain diameters, which quantifies the observable differences in the AFM images.

**Figure 25:** AFM topographical images of 1 x 1 µm² area showing the crystal grain microstructures of 20 nm thick Au films deposited by e-beam evaporation onto substrates of (a) Sapphire (b) Quartz and (c) Silica. Accompanying histograms show the distribution of the measured grain diameters.

In Figure 25, the average grain diameters, $d_G$, increased from 29.5 37.9 to 49.1 nm for the Au films on Sapphire, Quartz and Silica, respectively. This same trend of dependence of $d_G$ on the substrate was observed for Au films of all thicknesses. It was also notable that as $d_G$ increased, it corresponded to an increase in the standard deviation of grain sizes. In Figure 25 the standard deviation of the grain diameters, $\sigma_G$, increased from 16.9, 23.2 and 34.5 nm, for the Au films on Sapphire, Quartz and Silica, respectively. Despite the large standard deviation relative to the grain diameters, the large number of grains measured (over 500 per sample) results in a relatively small standard error associated with the measurements. Therefore the differences observed between the average grain diameter for films on different substrates can be deemed statistically significant.

The dependence of grain size on substrate can be explained by considering the interaction of Au atoms with the substrate during film fabrication.
One key factor affecting the Au microstructure is the lattice mismatch between the Au film and the substrate. Each material has a lattice constant that defines the lowest energy crystal lattice structure that the material can form. However, when the Au film deposits onto the substrate, any mismatch between lattice constants can induce strain in the Au film as it grows. Au has a unit cell of 4.07 Å in length [127] and this compares to the unit cells of Sapphire, Quartz and Silicon, which increase from 4.75 Å, 4.91 Å and 5.43 Å, respectively. The lattice constant for the Silica substrate will likely differ slightly from the value of 5.43 Å for Silicon, due to the 2-7 Å thick oxide layer that typically forms on its surface [109]. This increasing mismatch between Au and the substrate resulted in an increasing $d_G$ in the Au films on Sapphire, Quartz and Silica, respectively. This increasing lattice mismatch induced more strain on the Au film as it grew and lead to a release of the strain at the relatively weak grain boundaries, resulting in larger grains.

The most important substrate property that affects the Au grain microstructure is the surface energy. The wetting angle of arriving Au atoms is governed by the balance between attractive and cohesive forces of the Au and the substrate, which thereby determines the mechanism for film growth. Materials with high surface energies, such as Au, do not easily wet low surface energy substrates, such as the dielectrics, Sapphire and Quartz, and this results in a low contact angle of approximately 60-90° between Au and glass substrates [128]. This means that it is favourable for the Au atoms to interact with other Au atoms rather than with the substrate and thus adhesion of Au films to glass substrates is typically poor. This weak interaction favours Volmer-Weber growth whereby individual Au islands build up and form small grains.

The surface energy of Silica is greater than of the dielectrics and therefore there is a stronger attractive interaction between Au and Silica. This results in the spread of Au atoms on the substrate surface thus resulting in the formation of the larger grains observed in Figure 25, compared to on the other substrates.
4.2.2 Surface Roughness

To ascertain whether the substrate roughness contributes to grain growth and to the differences in Au grain microstructures observed in Figure 25, the surface roughness was determined for all Au films and all substrates. The surface roughness (Sq) is a measurement of the amplitude variations across the surface was therefore ascertained from six AFM topographical images as per the method described in Section 3.2.4. Example AFM images of the three bare substrates, Sapphire, Quartz and Silica surface are shown in Figure 26.

![AFM topographical images of the three bare substrates: (a) Sapphire, (b) Quartz, and (c) Silica.](image)

**Figure 26:** AFM topographical images of 1 x 1µm² area of the bare substrates (a) Sapphire (b) Quartz and (c) Silica.

The Sq data for each Au film of different thicknesses and on different substrates are shown in Figure 27, where the zero film thickness refers to the exposed substrate surface. The data in Figure 27 indicates that a smoother substrate surface results in a smoother Au film surface for all film thicknesses.

![Graph showing the surface roughness (Sq) of the substrates and Au films with different film thicknesses](image)

**Figure 27:** Surface Roughness (Sq) of the three substrates and the Au films with different film thicknesses on different substrates. Error bars represent the standard deviation of the roughness measurements made.

The Sq values of Sapphire, Quartz and Silica increased from 0.6, 1.1 to 1.8 nm, respectively and the Sq values of the Au films deposited onto these substrates
reflected this trend. The error bars represent a statistical significant difference in the surface roughness between the three substrate surfaces. This increasing surface roughness may also contribute to the increase in grain diameter for Au films on these substrates observed in Figure 25. A smoother substrate surface facilitates a higher surface diffusion rate of depositing Au atoms, which encourages the growth of isolated islands and results in smaller grains. The restriction of surface diffusion by a roughened substrate surface can result in increased coalescence between depositing Au atoms and thereby result in larger grains. The influence of the substrate roughness was most dominant for the thinnest Au films, where the interfacial interactions are most prominent. In Figure 27, there was overlap between error bars for the roughness measurements of some of the films deposited on the different substrates. Therefore there is insufficient evidence to conclude that the film roughness is dictated by the roughness of the substrate beneath.

The amplitude of the surface topography is dominated by the growth mechanism; Au films predominantly grow via the Volmer-Weber mechanism as described in Section 2.2.2. and therefore initially nucleate on the substrate surface and form islands. Films of 10 nm in thickness showed the greatest surface roughness in Figure 27 and this is because films are often discontinuous at this thickness. Discontinuity implies that islands of Au atoms form on the substrate surface and there may be an insufficient number of atoms to cause impingement between neighbouring islands [29]. This results in a large amplitude variation where the substrate is exposed and this leads to a larger perceived surface roughness. This is evident for the 10 nm thick Au films on Quartz and Silica, but the very low roughness of the Au films on Sapphire suggests that these films are continuous.

Thicker films become continuous, due to the arrival of a sufficient number of atoms to the substrate, which leads to the impingement of neighbouring islands and the energetically favourable mechanism of grain boundary formation. The formation of grain boundaries is energetically favourable due to the gain in interfacial energy between the grains, which exceeds the tensile stress within the grains. In order for grain boundaries to form, the islands must be within a distance, \( \Delta_{\text{max}} \), within which, the islands will spontaneously come together and
form a grain boundary. If the islands are within $\Delta_{\text{max}}$, the grain boundary energy, $\gamma_{\text{GB}}$, is less than the surface free energies of the individual islands, $\gamma_i$ [129].

$$\Delta_{\text{max}} = \left[ 2d_G (2\gamma_i - \gamma_{\text{GB}}) \frac{1-v_p}{E} \right]^{1/2}$$ \hspace{1cm} \text{Equation 35}

where the equation assumes that the grains are elastically isotropic and therefore $E$ is Young’s modulus and $v_p$ is Poisson’s ratio. The distance, $\Delta_{\text{max}}$, is also dependent on the grain radius, $\frac{1}{2}d_G$, and for a grain diameter of $d_G = 10$ nm, values of $\Delta_{\text{max}}$ were calculated as 0.55 nm. This effect was observed in Figure 27, where the surface roughness initially decreases with increasing film thickness. As the film thickness increases, the grain boundaries form and the film becomes continuous, thereby reducing the perceived surface roughness.

Figure 27 showed a decrease in surface roughness for films (10 - 25 nm), which results from the formation of continuous films, grain boundaries and the subsequent growth of the grain sizes with film thickness, as shown in the next section. This growth of grain size results in fewer grain boundaries and thus fewer variations in amplitude that is interpreted as surface roughness. The film thicknesses with the smoothest film surface were predominantly between 20 and 30 nm in thickness. The data in Figure 27 also shows that the surface roughness begins to increase again for the 90 nm thick films, which is considered in the next section.
4.2.3 Film Thickness

The effect of film thickness on the grain microstructure was also investigated. For Au films with thicknesses of 10, 20, 30 and 90 nm deposited on Silica, $d_G$ increased from 38.3, 49.2, 56.6 to 72.2 nm, respectively. However, for increasing film thickness deposited on Quartz and Sapphire, $d_G$ initially increased, but began to plateau for thicknesses above 25 nm, as shown in Figure 28.

![Graph showing the average grain diameter as a function of Au film thickness on Sapphire, Quartz and Silica substrates.](image)

According to the surface roughness measurements in Section 4.2.2, it is likely that the 10 nm thick Au films are discontinuous and consequently the measured grains are, in fact, small isolated islands. As the films thicken, they become continuous owing to the formation of grain boundaries. Thicker films become continuous and larger grains are formed via the aggregation of small grains or grain boundary movement \[130\]. The plateau of $d_G$ with the largest film thicknesses is explained by the Van der Drift model, whereby grains with higher vertical growth rate have a greater probability for survival and, as a result, large, well-oriented, stable grains are typically found for the thickest films \[131\].

So far, only the topography of the films has been considered. However, the grain microstructure is a 3D concept and therefore the growth of the grain microstructure throughout the film must be considered. The grain microstructure that develops as the film thickens is predominantly dependent on the temperature ratio between the substrate temperature, $T_s$, and the melting temperature of Au, $T_m$. According to the review by Kaiser that was presented in Section 2.2.2., the
films in this study result in a (Zone II) columnar grain microstructure [24]. Zone II relates to higher Au atom mobilities \((0.3 < T_s / T_m < 0.5)\), in which nucleation and growth occurs freely until impingement, thus forming granular columns [30].

Assuming a columnar microstructure, the aspect ratio (width : height) of the grains can be deduced from the graph in Figure 28. The aspect ratio was greatest for the thinnest films e.g. the aspect ratio was 4 for 10 nm thick Au films on Quartz and Silica and 2 for the Au film on Sapphire. As the film thickness increases, the aspect ratio decreases, until the aspect ratio reaches 0.3, 0.5 and 0.7 for 90 nm thick Au films on Sapphire, Quartz and Silica respectively. This fall in aspect ratio with increasing film thickness is due to the favourable epitaxial crystal growth in the vertical direction, thus increasing the grain height, but largely retaining the grain width.

### 4.2.4 Deposition Temperature

The effect of the deposition temperature on the grain microstructure was tested at deposition temperatures of 20, 200 and 450°C at a deposition rate of 15 nm / min. Figure 29 shows AFM topographical images of a 1 x 1 µm² area of the Au films deposited at 20, 200 and 450°C and are accompanied by histograms of the measured grain diameters. The films deposited at, 20, 200 and 450°C, resulted in values of \(d_G\) that increased from 29.1 nm \((\sigma_G = 15.6)\), 45.8 (18.3) to 61.9 (32.4), respectively.
Figure 29: Topographical AFM images of the grain microstructures of 20 nm thick Au films on Quartz fabricated at 15 nm / min and deposition temperatures of (a) 20 (b) 200 and (c) 450°C. Accompanying histograms show the distribution of grain diameters for each set of conditions.

The increase in $d_G$ and $\sigma_G$ with deposition temperature can be explained in terms of the kinetic energy of the incident Au atoms at the substrate surface. When the Au atoms impinge on the substrate surface, the atoms diffuse across the surface until an appropriate lattice site is found [57]. Surface diffusion is a thermally activated process and therefore at higher deposition temperatures the Au adatoms have an increased mobility and thus a greater diffusion distance on the surface, which results in a greater number of collisions and consequently larger grains. Additionally, higher deposition temperatures resulted in the Au atoms remaining in a molten phase for longer periods and thus impingement of neighbouring islands results in coalescence rather than grain boundary formation.
4.2.5 Deposition Rate

The effect of the deposition rate on the grain microstructure of the thin films was tested at deposition rates of 5, 15 and 30 nm / min at a deposition temperature of 20°C. Figure 30 shows AFM topographical images of a 1 x 1 µm$^2$ area of the Au films deposited at 5, 15 and 30 nm / min and are accompanied by histograms of the measured grain diameters. Values for $d_G$ for 20 nm films fabricated at 5, 15 and 30 nm / min deposition rates were 34.2 nm ($\sigma_G = 16.8$ nm), 29.1 (15.6) and 26.0 (13.2), respectively.

![AFM images of the grain microstructures of 20 nm thick Au films on Quartz fabricated at 20°C and deposition rates of (a) 5 (b) 15 and (c) 30 nm / min. Accompanying histograms show the distribution of grain diameters for each set of conditions.](image)

The increase in $d_G$ and $\sigma_G$ with decreasing deposition rate can be explained in terms of the number of nucleation sites forming on the substrate surface. With an increase in deposition rate, there is less time for the Au atoms to diffuse before the next atom arrives at the surface; hence there is an increase in the number of nucleation sites on the substrate surface in close proximity. As these nucleation sites grow via condensational growth into islands, they quickly impinge on a neighboring island and thus, on average, form smaller grains. It should be noted that the effect of these deposition rates on the film microstructure was not as significant as the effect of the applied deposition temperatures.
4.3 Factors Affecting Optical Properties

The purpose of fabricating and characterising the Au films was primarily to determine the impact of grain microstructure on laser-material interactions. In order to characterise these interactions, the portion of incident laser light that is reflected, transmitted and, most importantly, absorbed by the material is required. This requirement is complicated by the usage of thin films rather than bulk, since the optical properties of the film vary with both film thickness and wavelength. Additionally for thin films, the reflection, transmission and absorption of light does not occur at an interface, but over a depth comparable to the film thickness.

This section explores the optical properties of the Au films and determines the reflectance, transmittance and the absorptance of each film at three wavelengths that correspond to those available with the femtosecond laser; 343 nm (UV), 515 nm (Green) and 1030 nm (IR). The key factors that influence the optical properties of the Au films are then discussed in each section.

4.3.1 Data Collection

The reflectance, R, by each film was measured using the integrating sphere setup described in Section 3.3. The transmittance, T, through each film was calculated using Kidger Optical software, and the absorptance, A, by each film is then ascertained from \( A = 100 - T - R \).

It was not feasible to measure the transmittance through the Au film using the integrating sphere setup, due to the presence of the substrate. Therefore the transmittance values were ascertained using software that accounted for variations in the complex refractive index due to the film thickness and substrate. To verify that this software produced realistic data for the Au films, the reflectance data measured experimentally was compared to the data calculated
using the software. Figure 31 provides some examples of the comparison between the experimental reflectance data with the calculated reflectance for Au films on Quartz and Silica at the UV wavelength.

![Figure 31: Comparison of calculated (Kidger) and experimentally measured (Integrating Sphere) reflectances at 343 nm (UV) wavelength of Au films on (a) Quartz and (b) Silica. Error bars represent a standard deviation of 2.8% for the experimental measurement of the Au film reflectance.](image)

Figure 31 shows that there was excellent agreement between the calculated and experimental data for reflectance of the Au films (below 5% equating to a typical variation in absorbed fluence of 15 mJ cm$^{-2}$).

4.3.2 Film Thickness

The thickness of the Au film has the largest effect on their optical properties. Figure 32 provides an example of the variation in R, T and A of Au films in response to incident UV laser light due to the film thickness. Figure 32 shows that both R and A of Au films increase with the film thickness, which is compensated for by the decrease in T through the film.
The optical response of the 90 nm Au films, at all laser wavelengths, was representative of bulk Au, whereby the transmittance through the film was zero. Additionally, the reflectance and absorptance by the 90 nm films matched the values expected for bulk Au, irrespective of substrate. At UV, Green and IR laser wavelengths the reflectance by all 90 nm thick Au films was measured as 37%, 65% and 98%, respectively and the absorptance values were determined as 63%, 35% and 2%, respectively.

The most prominent change in the optical properties occurred for the films below 20 nm in thickness, where the films become increasingly transparent to the laser light. As the film becomes increasingly transparent, an increasing portion of light propagates through to the film/substrate interface, where the light may again be reflected, transmitted or absorbed.

4.3.3 Substrates

The presence of the substrate below the Au film can give rise to variations in the observed optical properties. The contribution of the substrate to the optical properties is dependent on the transmission of light through the film to the film/substrate interface, where it can be reflected, transmitted or absorbed by the
substrate. The influence of the substrate on the optical properties of the Au films is illustrated by Figure 33, in which the reflectance of the films below 30 nm in thickness begin to deviate from one another depending on the substrate.

![Figure 33](image_url)

Figure 33: (a) Reflectance of a range of Au film thicknesses deposited onto different substrates in response to incident UV laser light.

Figure 33 illustrates the same trend that was observed in the previous section; as the film thickness increases, the reflectance converges to the value expected for bulk Au (36%). The substrate becomes increasingly influential on the optical properties of thinner Au films. The contribution of the substrate to the measured reflectance is dependent on the quantity of light that reaches the film / substrate interface, which is dependant on two factors; the optical penetration depth and the transmittance through the Au film.

The optical penetration depth is characterised as $1 / \alpha$, where $\alpha$ is the absorption coefficient. At the laser wavelengths; UV, Green and IR, the optical penetration depths in Au are calculated as 14.85 nm, 19.39 nm and 11.59 nm, respectively: these values were calculated for bulk Au and it has been shown that the optical constants are only constant above a critical thickness, which is 25 nm for Au [132]. Based on these values, the laser light penetrates through the thinner Au films at all wavelengths, for which the optical properties varied the most with substrate.

Since the substrate also impacted on the optical properties for films with a thickness greater than the optical penetration depth, the transmittance through the
film was also an important factor. The transmittance through the Au films of different thicknesses was shown in Figure 32 and showed that the transmittance, T, through Au films below 90 nm in thickness was non-zero, hence a portion of the incident light penetrates through to the film / substrate interface. At the film/substrate interface the light can be reflected, transmitted or absorbed depending on the optical properties of the substrate. Both Sapphire and Quartz were highly transparent to the laser light at all wavelengths, whereas Silica resulted in high reflectivity and absorptivity of the light.

It should be noted the intensity associated with a femtosecond laser pulse can be sufficient to cause non-linear absorption of the laser by transparent materials, such as Sapphire and Quartz. The threshold intensity for non-linear ionization in dielectrics has been calculated as $\sim 10^{13}$ W cm$^{-2}$ [133], which is above the intensities applied in this study ($10^{12}$ W cm$^{-2}$).

It was evident from Figure 33 that the Au films on Silica resulted in a higher measured reflectance compared to Au films on other substrates. This significant difference in reflectance is due to the high reflectivity of the Silica compared to the reflectivity of Sapphire and Quartz. For example, at UV laser wavelength, the reflectivity of Sapphire, Quartz and Silica was measured as 14%, 8% and 55% respectively. Therefore, the measured reflectance of the Au film, R, is the sum of the reflected light at the air/film interface, $R_1$, combined with the reflected light at the film/substrate interface that penetrates through the film again, $R_2$. The reflections from the two interfaces can then interact either constructively or destructively depending on their phase relationship. The phase relationship depends on the laser wavelength of the light and the film thickness and optical properties, which determine the optical path lengths of these reflections. Constructive interference occurs when $2nd = i\lambda$ and destructive interference when $2nd = (i+1/2)\lambda$, where d is the film thickness and i is an integer. The reflectance therefore varies periodically with $1/\lambda$. Given that the film thicknesses (< 100 nm) were relatively small compared to the laser wavelengths used in this study, only part of a single oscillation is possible within the film and therefore the variations in reflectivity due to interference are minimal for all film thicknesses in this study. It should be noted that the Kidger optical software...
accounts for reflections at the film/substrate interface when calculating the transmission values for the Au films.

The resultant impact of the substrate on the absorptance by the Au film, A, was calculated by subtracting R and T from 100%. Figure 34 shows that the optical properties of the Au films diverge below 25 nm in thickness depending on the substrate. Figure 34 shows that the thinnest Au films on Silica resulted in the lowest absorptance compared to films on the other substrates, predominantly due to the high absorptivity and reflectivity of the Silica surface. Figure 34 also shows that the values for absorptance increased with film thickness on all substrates and converged to the same value for the 90 nm thick Au films of 62% at UV wavelength, irrespective of the substrate.

![Figure 34: Absorptance of laser energy by Au films of different thicknesses deposited on Sapphire, Quartz or Silica at UV laser wavelength](image-url)
4.3.4 Laser Wavelength

The portion of incident laser light that is reflected, transmitted or absorbed by a material is predominantly governed by the wavelength dependent, complex refractive index of the material. Figure 35 illustrates the significant variation in reflectance, transmittance and absorptance by a 20 nm Au film depending on the wavelength of the incident light.

![Graph showing optical response of a 20 nm Au film deposited on Quartz to incident laser light of UV, Green and IR wavelengths.](image)

**Figure 35:** Optical response of a 20 nm thick Au film deposited on Quartz to incident laser light of UV, Green and IR wavelengths. Optical response refers to the percentage of incident light that is reflected, transmitted or absorbed by the Au film.

Figure 35 illustrates that the absorptance by a 20 nm film is substantially higher at UV compared to Green and then IR wavelengths. This is due to the higher reflectance of the Au film to the IR wavelength and the higher transmittance through the film at the Green wavelength.

Commonly throughout the literature, the material response to a laser pulse is described at an applied laser fluence. In doing so, the differences observed at each laser wavelength, may result from differing absorbed laser fluences, rather than from the differing photon energy. Figure 35 illustrates the importance of adjusting the applied laser fluence to account for the portion of light that is reflected or transmitted by the material. The calculation of the absorbance by each Au film at each laser wavelength facilitates the comparison of laser ablation, nanoparticle generation and plasma generation at different laser wavelengths and the same laser fluence.
4.3.5 Grain Microstructure

Another factor that can affect the observed optical properties of thin films is the film surface roughness or grain microstructure. The different grain microstructures of the Au films were discussed in detail in Section 4.2. This section investigates whether smaller grains and therefore a greater density of grain boundaries, results in increased scattering and therefore a greater measured reflectance by the Au film. A set of five 20 nm thick Au films with different average grain diameters, \(d_G\), on Quartz was examined. The graph in Figure 36 shows how the reflectance of the films varied with grain diameter at the three laser wavelengths.

![Graph showing reflectance of Au films with different grain diameters](image)

Figure 36: Reflectance of 20 nm thick Au films with different average grain diameters and at 3 wavelengths. Error bars represent the standard deviation of the reflectance values measured.

Figure 36 shows that as the average grain diameter increases, and consequently the density of grain boundaries decreases, there is a small reduction in the reflectance. However, since the variation falls within the standard error bars, it cannot be deemed statistically significant.
4.4 Factors Affecting Laser Ablation Threshold

The laser ablation threshold fluence, \( \phi_{th} \), is a measurement used throughout the literature to characterise the material response to a laser pulse. The \( \phi_{th} \) can be deduced from the relationship between the diameter of ablated craters, \( D \), and the applied peak laser fluence, \( \phi_0 \) as per Equation 29.

The issue with the measurement of \( \phi_{th} \) for a material is that it refers to the applied laser fluence, rather than the absorbed laser fluence. It was shown in the previous section how the optical properties of a material vary with wavelength and consequently, the \( \phi_{th} \) of a material will also vary with wavelength. These variations are due to wavelength dependence of the optical properties, and not necessarily the wavelength dependence of the ablation threshold. Therefore this measurement may obscure any potential wavelength dependence of the ablation threshold of a material.

This Section attempts to overcome this issue by incorporating the absorbance of films with the measured values for \( \phi_{th} \). The key factors influencing the absorbed ablation threshold fluence for the Au films are then discussed.

4.4.1 Film Thickness

The applied laser ablation threshold fluence of each Au film, \( \phi_{th} \), was determined using the method laid out in Section 3.4.3. The \( \phi_{th} \) of each thin Au film was determined from a plot of the logarithm of the applied fluence, \( \phi \), against the squared diameter, \( D^2 \), of the ablated crater. The \( \phi_{th} \) of each film is determined from the point, at which, the extrapolated trendline crosses the x-axis. An example graph is shown in Figure 37 for Au films of different film thicknesses on a Silica substrate at the IR laser wavelength.
It was determined from Figure 37 that the $\phi_{th}$ of the Au films increased with film thickness at all laser wavelengths. The standard deviation of the $\phi_{th}$ for each film was determined to be 13.01 mJ cm$^{-2}$. From this result, it was still unclear whether a greater fluence was required to ablate thicker Au films, or whether the trend in Figure 37 is merely due to the variation in optical properties with film thickness. To clarify this point, the absorbed laser ablation threshold, $\phi_A$, was determined by subtracting the reflectance, $R$, and transmittance, $T$, from the $\phi_{th}$ values. The values of $\phi_{th}$ and $\phi_A$ for each Au film on Quartz at UV laser wavelength are shown in Figure 38.

Figure 38 shows an increase in both $\phi_{th}$ and $\phi_A$ with film thickness and therefore demonstrates that the variation in ablation threshold fluence with film thickness
is not dependant on the optical properties of the Au films. The analysis of all the films showed that there was an average increase in the absorbed laser fluence of 0.53 mJ cm$^{-2}$ per nanometer film thickness. The increase in ablation threshold fluence with film thickness is because a greater fluence is required to ablate a greater quantity of material.

4.4.2 Substrate

The next factor that contributed to the measured $\phi_{th}$ of the Au films was the substrate onto which they were deposited. The values for $\phi_{th}$ and $\phi_A$ were determined for all films to ascertain the contribution of the substrate to the ablation threshold fluence of the Au films. Figure 39 shows the measured $\phi_{th}$ and $\phi_A$ values of Au films of different film thicknesses deposited on Sapphire, Quartz and Silica at the Green wavelength.

![Figure 39](image_url)

**Figure 39:** The (a) applied and (b) absorbed ablation threshold fluences at Green laser wavelength of Au films of different thicknesses and on different substrates; Sapphire (S), Quartz (Qu) and Silica (Si).

Figure 39a illustrates the difference in $\phi_{th}$ for Au films on different substrates and Figure 39b shows that the values of $\phi_A$ are independent of the substrate. Therefore the increasing $\phi_{th}$ for Au films on Quartz, Sapphire and Silica observed in Figure 39a relates to the decreasing absorptance of Au films on these substrates, respectively. The absorptance by the Au films on Silica was low due to the high reflectivity and absorptivity of the Silica substrate. Therefore a greater applied fluence was required to achieve ablation of the Au films on Silica compared to on the other substrates. A notable observation is the convergence of
the values of $\phi_{th}$ for the 90 nm thick Au films, irrespective of substrate. This result once again implies that the 90 nm thick Au films behave as a bulk material.

The independence of $\phi_A$ from the substrate highlights the importance of accounting for the optical properties but also indicates that the thermal effects of the substrate have a minimal impact on the laser ablation threshold fluence of the Au film.

### 4.4.3 Fabrication Method

Another influential factor on the $\phi_{th}$ of the Au films was the deposition method for Au film fabrication. Figure 40 compares the values of $\phi_{th}$ and $\phi_A$ for a 20 nm Au film deposited on Quartz by e-beam evaporation and sputtering.

![Figure 40](image.png)

*Figure 40: Graph showing the difference in applied and absorbed ablation threshold fluences for a 20 nm thick Au film on Quartz when deposited by e-beam evaporation or sputtering.*

Figure 40 shows that the films deposited by sputtering had a substantially higher $\phi_{th}$ and $\phi_A$ than those deposited by e-beam evaporation by a factor of 4. It was proposed that the difference in $\phi_A$ was due to the different adhesion strengths of the Au films to the substrate. To test this idea, a simple qualitative adhesion test was carried out, as described in Section 3.2.5. Results showed that all films
deposited by e-beam evaporation were removed entirely by the tape, whereas all films deposited by sputtering remained entirely intact on the substrate.

Sputtering results in denser Au films with stronger adhesion to the substrate surface, compared to those deposited by e-beam evaporation. The stronger adhesion between the film and substrate is reflected in higher values of \( \phi_{th} \) and \( \phi_A \) for sputtered films than those fabricated by e-beam evaporation.

4.4.4 Laser Wavelength

The impact of the laser wavelength on the optical response of the Au film was evidenced in Section 4.3.4. Figure 41a shows the large variation in \( \phi_{th} \) for 20 nm thick Au films at different laser wavelengths and Figure 41b shows the small variation in \( \phi_A \) at different laser wavelengths.

![Figure 41](image)

*Figure 41*: (a) applied and (b) absorbed ablation threshold fluences at 3 laser wavelengths for 20 nm thick Au films on Quartz with different grain microstructures. Error bars represent the standard deviation for the measurement of the applied ablation threshold fluence.

Firstly, it is clear from Figure 41a that there is a statistically significant difference in \( \phi_{th} \) for films at different laser wavelengths. Figure 41b illustrates that by accounting for the film reflectance and transmittance, the values of \( \phi_A \) for each film thickness are comparable at all wavelengths and the values fall within the standard deviation error bars. This result also indicates that the large variations in \( \phi_{th} \) observed in Figure 41a are largely due to the varying optical properties between laser wavelengths, rather than thermal effects.
4.4.5 Grain Microstructure

The influence of the grain microstructure on $\phi_{th}$ and $\phi_A$ was monitored by comparing values of $\phi_{th}$ and $\phi_A$ for a set of five 20 nm thick Au films on Quartz with different average grain diameters, $d_G$. Figure 42a shows the dependence of $\phi_{th}$ on the average grain diameter, $d_G$ and Figure 42b shows the dependence of $\phi_A$ on $d_G$.

![Figure 42](image)

Figure 42: (a) applied and (b) absorbed ablation threshold fluences of 20 nm Au films on Quartz at different laser wavelengths and with different average grain diameters. The error bars represent the standard deviation of measured applied ablation threshold values for each film.

Figure 42a shows that an increase in average grain diameter, and consequently a decrease in grain boundary density, results in a decrease in $\phi_{th}$. This trend is predominantly observed for the smallest grain diameters, which equates to the greatest grain boundary density. The values for $\phi_{th}$ appear to plateau for the largest grains. Figure 42b presents the values for $\phi_A$ and shows that the variation in the ablation threshold fluence with the grain size is attributable to the increased reflectance due to the scattering of incident light by the grain boundaries.
4.5 Laser Ablation Threshold Summary

The results in this section evidence the importance of accounting for the optical properties when comparing the laser ablation of different samples. The variation of $\phi_{th}$ of Au films with different substrates, grain microstructures or at different wavelengths were all attributable to the variation in the absorbance by the Au films. Therefore the absorbed ablation threshold fluence, $\phi_A$, was found to be independent of the substrate, the grain microstructure or the wavelength. This informs that the ablation threshold fluence for a material is material dependent for a femtosecond laser pulse.

The only factors that resulted in a variation of $\phi_A$ was the fabrication method and the film thickness. The fabrication methods of e-beam evaporation and sputtering resulted in different adhesion strengths between the film and the substrate. A stronger adhesion between the film and the substrate resulted in a higher $\phi_{th}$ and $\phi_A$.

For bulk Au, the $\phi_{th}$ does not vary with thickness since the ablated depth is governed by the thermal penetration depth and the ballistic electron depth [41]. However, for thin films (<100 nm) the film thickness is shorter than these depths, and therefore the heated volume is largely confined by the beam diameter and the film thickness. For this reason, the laser energy absorbed by the films is confined to different volumes depending on the film thickness. This resulted in an increase in $\phi_A$ with film thickness, where a greater fluence was required to ablate a greater volume of material.

The relationship between $\phi_A$ and the film thickness is shown for a range of film thicknesses on different substrates in Figure 43.
Figure 43: Variation in absorbed ablation threshold fluence, $\phi_A$, for Au films with different thicknesses and different laser wavelengths.

Assuming a linear relationship in Figure 43, the trendline was extrapolated back to $x = 0$ and $\phi_A$ was found to be $4.62 \text{ mJ cm}^{-2}$, across all three wavelengths. Assuming a density of $19,320 \text{ Kg m}^{-3}$, this absorbed fluence equated to $7.95 \times 10^{-19} \text{ J}$ or $4.97 \text{ eV}$ per atom. This value exceeds the work function of Au, which for bulk Au has been determined within the range of 4.7 - 5.1 eV. Although a simple calculation correlating to the laser ablation of a film with thickness zero, it is indicative that in order for ablation to ensue, sufficient laser energy must be absorbed by each atom to surpass the work function. Since the laser energy interacts primarily with the free electrons in a material, it is important to consider the electronic system of Au. The outer electronic system of Au is described by $5d^{10}6s^1$. Therefore the density of free electrons per unit volume is determined as a single free electron per atom and is therefore $5.9 \times 10^{28} \text{ m}^{-3}$. When an electron absorbs sufficient energy to exceed the work function of the material, it is removed from the material. If a sufficient density of single electrons per atom are removed from a material, then ablation can ensue.

This calculated fluence for ablation per atom does not account for the method of delivery of this energy. For example, three laser wavelengths were used, which have different photon energies; UV, Green and IR wavelengths have photon energies of 3.62 eV, 2.41 eV and 1.21 eV, respectively. Therefore, for each electron to absorb sufficient energy to exceed the work function of the material, two possible mechanisms can ensue; Multiphoton photoemission or thermionic...
emission. These mechanisms will be discussed in further detail in Chapter 6, where the electron emission from the Au films will be discussed.

From Figure 43 it was also determined that an additional $0.45 \pm 0.03 \text{ mJ cm}^{-2}$ was required to ablate each additional nanometer of film thickness. This equates to a value of $4.46 \text{ kJ cm}^{-3}$, which was then compared to the enthalpies of Au for melting and evaporation, which have values of $2.86$ and $9.25 \text{ kJ cm}^{-3}$, respectively [134]. Given the lack of information for thin films with thicknesses between 30 and 90 nm, a trendline was also produced for the absorbed ablation threshold fluence for films with thicknesses of 10-30 nm only. This resulted in a gradient of 0.74, which equated to a value of $7.38 \text{ kJ cm}^{-3}$. This informs that at the $\phi_A$ of the Au films (10-90 nm in thickness), the film has sufficient energy to melt, but not to vaporise.
4.6 Conclusions

The main conclusions derived in this Chapter are given below:

- **The grain microstructure of thin Au films can be controlled by selecting the appropriate substrate, fabrication conditions and the film thickness.**

  The average grain diameter, $d_G$, was ascertained from the topographical images of the films. The grain microstructure is dependent on the film growth mechanism which is governed by a number of factors during fabrication. The surface diffusion of arriving Au atoms is hindered by a high substrate surface roughness and low deposition rate, which therefore leads to larger Au grains. High deposition temperatures results in high Au mobility on the surface, leading to collisions, coalescence and larger grains. A high wetting angle of the Au atoms on the substrate is governed by the relative surface energies and Young’s equation. A larger wetting angle occurs on Silica compared to Sapphire and Quartz, thereby resulted in larger grains. Finally, increasing the film thickness was found to follow the Van der Drift model, in which the grain diameter initially increases with film thickness before reaching a plateau.

- **The optical properties of thin Au films are impacted by the film thickness, substrate and grain microstructure at different laser wavelengths**

  Films of 90 nm thickness displayed optical properties representative of bulk Au. Whereas thinner Au films became increasingly transparent to the laser light and consequently the optical properties of the substrate became increasingly influential. The impact of the grain microstructure on the measured reflectance was not statistically significant. The absorption of laser light by the Au films decreased from UV to Green and to IR.
• The absorbed ablation threshold is dependent on the adhesion strength and the film thickness, but independent of grain microstructure, laser wavelength and substrate.

The literature commonly refers to the ablation threshold fluence of a material as the fluence applied to the material to achieve ablation. Due to variations in optical properties of materials, the ablation threshold fluence varies with substrate, grain microstructure and laser wavelength. However, by accounting for the variations in optical properties, the absorbed ablation threshold is independent of these factors. For example, the absorbed ablation threshold fluences were the same for films of equal thickness with a standard deviation of 3.67 mJ cm$^{-2}$. The absorbed ablation threshold fluence of Au films was found to increase with adhesion strength between the film and substrate and also with the film thickness.

• The absorbed laser ablation threshold fluence per atom is equivalent to the work function of Au

The linear relationship between the absorbed ablation threshold fluence with film thickness was extrapolated to find the threshold fluence required to achieve ablation of Au films. A value of 4.97 eV per atom was determined, which exceeded the work function of Au, which lies between 4.7 – 5.1 eV. Therefore it was established that the emission of a sufficient number of electrons must be achieved in order for ablation to ensue.

• The absorbed laser ablation threshold fluence falls between the melting and vaporisation enthalpies

The linear relationship between the absorbed ablation threshold fluence with film thickness was used to determine that 4.46 kJ cm$^{-3}$ was required to achieved ablation of Au films. This value falls within the enthalpies of melting and evaporation for Au, which are 2.86 and 9.25 kJ cm$^{-3}$, respectively.
Chapter 5
Grain – Nanoparticle Size Relationship

5.1 Introduction

Previous studies had shown that laser ablation of materials can lead to the production of nanoparticle debris [11, 46, 135, 136]. Various material and laser parameters had been investigated to ascertain their influence on the size distribution of nanoparticles that result [7, 11, 16, 124]. During a literature review, two areas of interest were identified for investigation in this study; the effect of the grain microstructure of thin films and the effect of the laser wavelength on laser ablation and nanoparticle generation.

This Chapter therefore presents the results of a study into whether a relationship exists between the size of the film grains and the size of nanoparticles generated during femtosecond laser ablation of thin Au films. This Chapter also presents the results of ablation and nanoparticle generation at three laser wavelengths at the same absorbed laser fluence.

Chapter 4 presented the characterisation of the grain microstructures of a range of Au films. The optical properties of each film was also calculated and presented in the previous chapter. From this data it was possible to laser ablate
each film at an equal absorbed fluence and measure the nanoparticles that were generated. The size of the nanoparticles were measured from SEM images and compared to the size of the grains established in Chapter 4. Nanoparticles were generated from each film at three laser wavelengths and at equal laser fluences. Previous studies had only investigated laser ablation at different wavelengths using a single applied fluence and did not account for the variation of the material optical properties, thereby obscuring any potential impact of the photon energy [46, 97].

The key objectives of this Chapter are:

- Establish a method to compare laser generation of nanoparticles at different laser wavelengths, whereby the absorbed laser fluence is the same for all Au films.

- Establish whether a relationship exists between the size of the Au grain microstructure and the size of the nanoparticles that are generated during femtosecond laser ablation.

- Investigate the influence of laser wavelength (photon energy) on the ablation mechanism and generation of nanoparticles by maintaining the same absorbed laser fluence at each laser wavelength.
5.2 Laser Ablation

In order to accurately compare laser ablation and nanoparticle generation from different Au films and at different laser wavelengths, it was imperative to account for the variation in optical properties shown in Chapter 4. If the absorbed fluence by each film was equal, the mechanisms for ablation and nanoparticle generation could be justly compared.

5.2.1 Laser Fluence for Nanoparticle Generation

Prior to accumulating the optical data presented in Chapter 4, a method was devised to compare nanoparticle generation at different laser wavelengths. The intention of the method was to generate a comparable laser-material interaction at each laser wavelength. The method was based on achieving ablated craters of the same size at each laser wavelength, relative to the Gaussian beam diameter.

Figure 44 shows the intensity distribution of a Gaussian laser beam. When a fluence, $\phi$, is applied to a material that exceeds the ablation threshold fluence, $\phi_{th}$, damage to the surface will be induced. The fluence selected for this comparison study of laser generation of nanoparticles at different wavelengths was $\phi_{NP}$, at which the diameter of the ablated crater, $D$, equalled the Gaussian beam diameter, $2\omega_0$, at each laser wavelength. The Gaussian beam diameter, $2\omega_0$, is characteristic of the laser and independent of the material.
Figure 44: Image showing the distribution of the fluence, \( \phi \), with respect to the radius, \( r \), of a Gaussian laser beam. \( \phi_0 \) represents the peak fluence. \( \phi_{th} \) represents the threshold fluence for laser ablation. \( 2\omega_0 \) represents the \( 1/e^2 \) diameter of the distribution, which relates to the diameter of the crater ablated for nanoparticle generation, \( \phi_{NP} \).

At UV, Green and IR wavelengths the Gaussian beam diameter, \( 2\omega_0 \), was determined as \( 30.8 \pm 0.9 \, \mu m \), \( 33 \pm 1.0 \, \mu m \) and \( 50.8 \pm 3.4 \, \mu m \), respectively. The applied laser fluence to generate a crater with \( D = 2\omega_0 \) was termed the laser fluence for nanoparticle generation, \( \phi_{NP} \) and was calculated for each film and wavelength. Importantly, the values of \( \phi_{NP} \) are above the ablation threshold fluence of the film and resulted in the generation of nanoparticles, without causing damage to the substrate beneath.

Following the development of this method, the optical properties of the films at different wavelengths were measured and have been presented in Chapter 4. As was the case with the ablation threshold fluence, \( \phi_{th} \), described in Chapter 4, the values of \( \phi_{NP} \) also varied with deposition method, film thickness, substrate and laser wavelength. For example, a 20 nm thick Au film sputtered onto Quartz, the average values of \( \phi_{NP} \) were 0.77, 1.12 and 2.08 J cm\(^{-2} \) at UV, Green and IR laser wavelengths, respectively. The standard deviations for these values were 0.012, 0.026 and 0.031 J cm\(^{-2} \), respectively.
This large variation in $\phi_{NP}$ with laser wavelength was later accounted for by considering the absorptivity of the Au films at different laser wavelengths. The absorptivity of the Au film at UV, Green and IR wavelengths was 38%, 28% and 14%, respectively, thus giving rise to an average absorbed fluences of 300 mJ cm$^{-2}$ at all wavelengths with a standard deviation of 12.5 mJ cm$^{-2}$, as illustrated by Figure 45. This result again highlights the importance of accounting for these optical property variations when comparing laser ablation at different laser wavelengths.

![Figure 45](image-url): The applied and absorbed laser fluence for nanoparticle generation from a 20 nm Au film on Quartz at UV, Green and IR laser wavelengths. Error bars represent the standard deviation associated with the determination of the applied threshold fluence for nanoparticle generation.

5.2.2 Crater Profiles

In this study it was imperative to ensure that the laser ablation process was confined to the thin film and that no damage was incurred by the substrate below. The absorption by each substrate at each wavelength was calculated from the measured reflectivity and the calculated transmittance in Chapter 4. The data had shown that Quartz and Sapphire have low absorptivity (< 5 %) at all the laser wavelengths applied in this study. Contrarily, the substrate Silica had a substantially higher absorptivity (> 50%) at all wavelengths. Consequently, it was imperative to determine that the application of $\phi_{NP}$ to the Au film did not result in physical damage or ablation of the substrate beneath and all
nanoparticles comprised solely of Au. This was verified using AFM by imaging the topography of the ablated crater and then determining the profile across it. The cross-sectional profiles showed smooth surface across the ablated crater, implying that no physical damage to the substrate was incurred. An example of such an image and profile of an Au film on Quartz is shown in Figure 46.

Figure 46: AFM image of a laser ablated crater of an Au film on Quartz and an accompanying cross section illustrating that no damage of the substrate occurred following UV laser ablation.

The profiles showed that there was no damage to the any of the substrates at $\phi_{\text{NP}}$ and that the entire thickness of film was removed with a single laser pulse. All $\phi_{\text{NP}}$ values for Au films fell far below the damage thresholds of the substrates and no damage to the substrate was observed.

The profile of the crater shown in Figure 46 also shows that some of the ablated material accumulates at the edge of the crater, whilst the remaining volume of material ablated is found as nanoparticles deposited in and around the crater, and it is this debris that is of interest in this study.

5.3 Nanoparticle Generation

Nanoparticles were generated following the femtosecond laser ablation of each Au film at the respective fluence, $\phi_{\text{NP}}$. The re-deposited nanoparticles were imaged using an SEM and the diameter of over 250 nanoparticles were measured using the method described in Section 3.5. The mean diameter, $d_G$, and the standard deviation of the diameters, $\sigma_G$, were measured for each film and set of conditions. The influential factors that affected the size distribution of nanoparticles are discussed in this Section.
5.3.1 Influence of the Substrate

The size distributions of nanoparticles were compared for Au films on different substrates of Sapphire, Quartz and Silica. The nanoparticles with the smallest $d_{NP}$ were generated from Au films on Sapphire, then Quartz and the largest from Au films on Silica. This is illustrated by the SEM images of nanoparticles generated from 20 nm thick Au films on Saphhire, Quartz and Silica, respectively, in Figure 47. The $d_{NP}$ of these nanoparticles were 8.6 nm, 18.4 nm and 22.6 nm, respectively. The accompanying histograms in Figure 47 quantify the distribution in nanoparticle diameters measured for each film. The histograms show that as $d_{NP}$ increases, $\sigma_{NP}$ broadens.

Figure 47: SEM images of Au nanoparticles generated during UV laser ablation of 20 nm thick Au films on (a) Sapphire (b) Quartz and (c) Silica with accompanying histograms of nanoparticle diameters.

The variation in nanoparticle sizes was potentially attributable to several different factors; firstly the re-deposition of nanoparticles onto the exposed substrate surface introduces differing surface energies and thus different wetting angles that were first discussed in Section 2.2.1 during the fabrication of the films. The differing surface energies of the substrates are significant if the re-depositing nanoparticles were still in a molten state. A variation in wetting angle can result in a variation in the perceived nanoparticle diameters. However, images evidence spherical nanoparticles that indicate that re-solidification has taken place prior to their re-deposition on the exposed substrate surface. The re-
deposition of the nanoparticles occurs over sufficiently long periods that re-solidification occurs prior to re-deposition (Section 3.6.1). To verify that the re-deposited nanoparticles were indeed spherical, the SEM was used to view the sample at a tilted angle. No images were recorded, though there was no visible wetting between the Au nanoparticles and the substrates. Therefore the surface energy was not considered a key influence on the nanoparticle size.

Alternatively, the size of the nanoparticles could be linked to the size of the grain microstructures, which mimicked the same trend observed in Figure 47 i.e. a larger d_G gave rise to a larger d_NP. Consequently, the relationship between the grain microstructure and nanoparticles warranted further exploration.

### 5.3.2 Influence of Grain Diameter

To explore the potential relationship between d_G and d_NP, a set of five 20 nm thick films were fabricated with different d_G and all deposited on the same substrate, Quartz. The films varied only in their grain microstructure, owing to the conditions employed during fabrication. The average grain diameter, d_G, was established for each film in Chapter 4 and was compared to the average nanoparticle diameter, d_NP, generated following a UV laser pulse at \( \phi_{np} \). An example of the nanoparticles generated from 20 nm thick Au films on Quartz with a d_G of 33 nm (\( \sigma = 16 \)) and 62 nm (\( \sigma = 32 \)) are shown in Figure 48. The d_NP of the nanoparticles shown were 11 nm (\( \sigma = 7 \)) and 25 nm (\( \sigma = 24 \)), respectively.
Since these nanoparticles were generated from the same film thickness and re-deposited onto the same substrate, this data supported the hypothesis that $d_{NP}$ was linked to $d_G$ for UV laser ablation of Au films.

The comparison of the average grain diameter, $d_G$, with the average nanoparticle diameter, $d_{NP}$, depended on the fact that these mean values were representative of the true population means. The confidence intervals for the samples were therefore evaluated. Where sampling of grain sizes was repeated, the calculated confidence interval ($d_G \pm 2.85 \text{ nm}$) would encompass the true population mean grain diameter, 95 % of the time. Where sampling of nanoparticle sizes was repeated, the calculated confidence interval ($d_{NP} \pm 2.07 \text{ nm}$) would encompass the true population mean nanoparticle diameter 95 % of the time. Therefore the mean values determined for each grain sample set, $d_G$, or nanoparticle sample set, $d_{NP}$, can be deemed representative of the mean of the population. Therefore the difference in $d_{NP}$ is deemed statistically significant since the only difference between the ablated films was the grain microstructure.
5.3.3 Influence of Film Thickness

Another factor that impacted on the nanoparticle size was the film thickness. The values of $d_{NP}$ generated from Au films of 10, 20, 30 and 90 nm thicknesses on Sapphire increased from 5.4, 8.6 10.4 to 13.4 nm, respectively. With an increasing $d_{NP}$, there was also an increase in the standard deviation of nanoparticle diameters measured, which is reflected in the histograms of the nanoparticle diameters in Figure 49.

![Figure 49: Histograms of the measured diameters of nanoparticles generated during UV laser ablation of Au films with thicknesses of 10, 20, 30 and 90 nm.](image)

The increase in $d_{NP}$ with film thickness was initially attributed to the confinement of the laser-material interaction to the dimensions of the film and the laser beam [11, 46]. Recent modeling studies have compared the thermal distributions, 40 picoseconds after a fs laser pulse, throughout an Au film of 100 nm thickness and bulk Au and found that the temperature varied by only 50 K in a 100 nm film and 1400 K over a 200 nm depth in the bulk Au [46]. This quasi-uniformity in Au films of 100 nm thickness (and less) is due to the motion of ballistic electrons in
Au films, which can travel approximately 100 nm owing to the mean free path of an electron in Au calculated to be 117 nm [41]. This study has compared films of thicknesses within the ballistic electron depth, which according to this model would suggest that the thermal distribution throughout films of 10 – 90 nm in thickness is quasi-uniform. Therefore the differences observed between nanoparticles generated from sub-100 nm thick films were not attributable to differing thermal distributions in the film and hence must be attributed to another factor.

It was noted in Chapter 4 that there was an increase in \( d_G \) with film thickness, which could potentially also contribute to this observed phenomenon. It was therefore important to establish whether it was just \( d_G \) that governed the nanoparticle size of whether the film thickness was also a contributing factor. The ratio of \( d_G \) to \( d_{\text{NP}} \) was compared to the film thickness and the results are presented in Figure 50.

![Figure 50](image)

**Figure 50:** Ratio of diameters of grains and nanoparticles from different Au film thicknesses.

Figure 50 indicates that despite accounting for the increase in \( d_G \) with film thickness, the \( d_{\text{NP}} \) still increased with the film thickness. This result informs that it is not solely \( d_G \) that influences \( d_{\text{NP}} \) and confirms that the film thickness is also a contributory factor. Given these results, a more appropriate relationship to explore was to compare the volume of the grains to the volume of the nanoparticles, as shown in the next section.
5.4 Grain – Nanoparticle Relationship

The previous section identified the contribution of the grain diameter and the film thickness to the size of the nanoparticles that formed. Therefore, this Section explores the relationship between the volume of the film grains with the volume of the nanoparticles that form. This relationship was termed the grain-nanoparticle relationship.

5.4.1 Grain and Nanoparticle Volume

The SEM images of the nanoparticles showed largely spherical nanoparticles and consequently, their mean spherical volumes, $V_{NP}$, were determined from their measured diameters, as described in Section 3.6.3.

The values for the mean grain volume, $V_G$, were more complex to evaluate but were estimated using the film topography and film thickness as per 3.2.3. The topography of the Au thin film surface was imaged using AFM, from which, the surface area of the grains were determined. Perpendicular to the substrate surface, the microstructure depends on the fabrication conditions and particularly the temperature ratio between the Au melting temperature, $T_m$, and the substrate temperature during fabrication, $T_s$. Using the model set out by Kaiser and allowing for melting-point depression due to film thickness, it was determined that the microstructure of the films were most likely to be columnar [24]. Therefore the average volume of the grains was determined as the spherical surface area of the grains multiplied by the film thickness.

5.4.2 Grain-Nanoparticle Relationship

The volume relationship between grains and nanoparticles was tested for four Au films on Sapphire of 10, 20, 30 and 90 nm thickness. The average volume of the grains, $V_G$, was compared to the average volume of the nanoparticles, $V_{NP}$,
generated following a single UV laser pulse and the relationship is shown in Figure 51. It was evident from Figure 51 that a strong relationship existed between $V_G$ and $V_{NP}$. A linear trendline resulted in an $R^2$ value of 0.97.

![Figure 51: Average volume relationship between grains and nanoparticles for a set of 10, 20, 30 and 90 nm thick Au films on Sapphire at UV laser wavelength.](image)

To explore this relationship further, a set of 20 nm Au films with 8 different grain microstructures was used. By eliminating the contribution of film thickness, it would be possible to establish the influence of the grain microstructure on the nanoparticles that were generated. Figure 52 shows the relationship between $V_G$ and $V_{NP}$ for the 20 nm thick Au films following UV laser ablation. The standard error was determined for each grain and nanoparticle sample set and is presented as the x and y axis error bars.

![Figure 52: Graph of the linear relationship of average grain volume of eight 20 nm thick Au films with the average volume of the nanoparticles generated during a UV femtosecond laser pulse. The error bars represent the standard errors for the calculation of the average volumes.](image)

A linear trend was observed, with an $R^2$ value of 0.94, which implied a strong relationship between the grain microstructure with the nanoparticles that were
generated. The large number of grain and nanoparticles measured resulted in narrow standard errors associated with the calculation of the mean diameters. The strong linear trend and limited overlap of error bars in Figure 52 confirms the existence of the grain-nanoparticle relationship during UV femtosecond laser ablation of thin Au films.

5.4.3 Laser Wavelength Dependence

The existence of the Grain-Nanoparticle relationship had been confirmed at the UV laser wavelength. The Grain-Nanoparticle relationship was then compared at three laser wavelengths; 343 nm (UV), 515 nm (Green) and 1030 nm (IR) at the respective $\phi_{NP}$, as shown in Figure 53. The error bars shown in Figure 53(a) represent the standard error values for the grain and nanoparticle volumes. Error bars were omitted in Figure 53(b) due to logarithmic scale, but no overlap between standard error bars was observed.

![Figure 53](image)

*Figure 53:* Volume relationship between the grain of the 20 nm Au film and the Au nanoparticles generated during laser ablation at (a) UV and Green wavelengths (Blue diamond and Green square, respectively) and (b) IR wavelength (red triangles). Note logarithmic scale on vertical axis in (b). Error bars represent the standard error associated with the data point.

There were two key findings from Figure 53; The first is that the Grain-Nanoparticle relationship shows a linear correlation between $V_G$ and $V_{NP}$ at UV and Green wavelengths with an $R^2$ value of 0.906, whereas at IR wavelength the $R^2 \approx 0$. The second finding is the statistically significant similarity in the size of nanoparticles generated at UV and Green wavelengths, which is supported by the overlap in standard error bars for nanoparticles generated from the same film. It is also statistically significant that the nanoparticles generated during UV or
Green ablation are not comparable in size with those generated during IR laser ablation.

The equation from the trendline in Figure 53a indicated that, on average, seven average sized nanoparticles were generated per average sized grain at UV and Green wavelengths. The exact number and size of measured nanoparticles generated can be affected by factors, such as collection method, as discussed in Chapter 3. However, since the method of collection was the same for all films and wavelengths comparisons within the study can be drawn. For this reason, however, the numerical relationship may differ if a different method of collection was utilized. To determine the extent of bias incurred by the chosen collection method, the Average Distribution of nanoparticles (standard deviation / average diameter) was compared to a collection method favoured in other studies, whereby a substrate is orientated above the surface and parallel to the target surface \[104\]. For example, Amoruso found the Average Distribution of Au nanoparticles generated during femtosecond laser ablation fell between 0.5 and 1 and in this study the Average Distributions were 0.85, 0.59 and 0.72 for nanoparticles generated during UV, Green and IR ablation, respectively.

Another observation from Figure 53 was that the choice of substrate and the fabrication method affected neither the existence, nor the magnitude, of the Grain-Nanoparticle relationship. The substrate and fabrication method was highly influential in the grain microstructure of the Au film that formed, as well as the optical properties, but these were accounted for in \(\phi_{NP}\) and the effect of these factors on the ablation mechanism and nanoparticle formation appear minimal.

Most importantly, it was evident from the results presented in Figure 53 that despite the adaptation of the applied laser fluence, \(\phi_{NP}\), for each film and laser wavelength to overcome differences in optical properties, there was still a wavelength dependant factor impacting on nanoparticle generation during laser ablation.
5.5 Photon Absorption

The linear Grain-Nanoparticle relationship existed following the absorption of a laser pulse at UV and Green wavelengths, but not at the IR wavelength. Since the applied laser fluence was adapted to account for differences in film optical properties at different wavelengths, this result implied that there were potentially differing absorption and ablation mechanisms occurring depending on the photon energy applied in the laser pulse. This section now draws on information generated by computational models that have explored non-equilibrium dynamics and the impact of photon energy on laser absorption by noble metals, such as Au.

5.5.1 Electronic System of Gold

The absorption of laser energy occurs predominantly via the electronic system and in particular by the electrons near the Fermi level. For Au, the electronic structure is $5d^{10}6s^1$ with the Fermi level dissecting the half-occupied 6s band. An image of the electron density of states (5d and 6s bands) of Au has been extracted from [48] and shown in Figure 54. The image includes the calculated Fermi distribution functions for three electron temperatures [48]. It should be noted that despite many physical properties changing on the nanoscale, the electronic band structure remains largely unaltered until below 5 nm in size, when Au ceases to behave as a noble metal [137].
The excitation of electrons is dependent on the availability of energy states following the absorption of a photon of a given energy. The energy of the absorbed photon therefore dictates the electronic response of the material, which consequently impacts on the lattice response, ablation mechanism and finally nanoparticle generation.

5.5.2 Non-Equilibrium Dynamics

The TTM is a vital model for understanding the response of electronic and lattice systems to an ultra-short laser pulse. However, in Section 2.3.5 some of the limitations of the model were introduced. Recent models have moved to combine non-equilibrium dynamics (NED) with the TTM, which has resulted in significant changes to the predicted absorption and heating processes [138]. For example, the TTM assumes two conditions that are shown to significantly differ when NED is accounted for. Firstly, that the electrons thermalise to a single temperature $T_e$ following the thermalisation time, $\tau_{ee}$. Secondly, that $G_{ep}$ is a constant.

Following the absorption of laser energy by the electrons, they will energetically decay for a time defined by $\tau_{ee}$ through inelastic collisions with other electrons.
However, following $\tau_{ee}$, the distribution function of electrons remains in non-equilibrium for a further period due to the generation of secondary electrons, before finally achieving a Fermi distribution [53]. The electrons may therefore take between 100 fs up to a picosecond to achieve thermalisation [139]. Therefore for time-scales shorter than 1 ps, the use of a single electron temperature, $T_e$, in the TTM is contentious. Models have also shown that the electron-phonon coupling factor, $G_{ep}$, can vary significantly when the density of states (DOS) of a material is taken into account [40]. The TTM also assumes that electron-electron and electron-phonon interactions are independent of temperature. Whereas, the temperature can have a significant impact on the behaviour of the material, with respect to its electronic structure and collision frequency.

Computational studies have attempted to model these non-equilibrium electronic and phononic dynamics following the absorption of an ultra-short laser pulse to better fit experimental data. Leading this field, is Rethfeld, who developed a kinetic model to include Boltzmann collision integrals and distribution functions of the electrons and phonons, to describe the excitation and relaxation of the electronic system and the coupling of its energy to the lattice system [53, 138, 140]. By accounting for the NED in the model, it was possible to model the thermal distribution in aluminium at different temperatures that agreed more precisely with the experimental data than the TTM alone [53]. The most significant outcome of this model was the insight into the importance of the density of states (DOS) on the material response to an ultra-short laser pulse, which became evident with the modeling of noble metals, such as Au and Ni. In such computational models, the DOS is typically accounted for by applying an effective one-band model, in which an averaged isotropic dispersion relation is derived [138]. It was determined that the excitation of the d-band electrons could result in substantial changes in the electron temperatures, heat capacities and consequently the electron-phonon coupling factor.
5.5.3 Electronic Response of Gold

Lin and Zhigilei built on this result and developed a combined Atomistic-Continuum computational model, which joined the classical Molecular Dynamics method with VASP and the TTM model in order to identify the influence of d-band excitation in Au on the thermal distribution in a 20 nm thick Au film [48]. The key aspects of these models were discussed in the Section 2.3.5. The model was used to investigate the effect of the electron DOS and the temperature dependence of the electron-phonon coupling, electron heat capacity and thermal conductivity, on the material response to incident femtosecond laser pulses. The electronic DOS was determined using the Vienna Ab-initio Simulation package (VASP).

Lin and Zhigilei investigated whether the excitation of d-band electrons in Au resulted in a different electron thermal distribution, compared to when d-band excitation was not achieved. The photon energy required to achieve excitation of d-band electrons to the Fermi level is described as the interband transition threshold (ITT) and varies across the Fermi surface by 1.8 - 2.4 eV in Au [40, 138, 141-143]. If the photon energy absorbed by Au is less than the ITT, then absorption is only by the 6s electrons via intraband absorption and the d-band is unperturbed [48]. If the photon energy absorbed by Au exceeds ITT, then absorption can also be achieved by the 5d electrons via interband absorption.

The absorption of the photon energy by the electronic system is also dependent on the electronic heat capacity. Typically, the estimation of the electronic heat capacity, \( C_e \) is achieved through the Sommerfeld linear approximation, \( C_e(T_e) = \gamma T_e \). Values for \( \gamma \) have been calculated for Au as 62.7 J m\(^{-3}\) K\(^{-2}\) [144]. The electronic heat capacity can be derived from the total energy density, with respect to the electron temperature.
\[ C_e(T_e) = \int_0^\infty \frac{df(E, \mu(T_e))}{dT} g(E) E \, dE \quad \text{Equation 36} \]

where \( g(E) \) is the density of states (DOS), \( \mu \) is the chemical potential and \( f(E, \mu(T_e), T_e) \) is the Fermi distribution function described by the following equation.

\[ f(E) = \frac{1}{e^{(E - \mu)/k_B T} + 1} \quad \text{Equation 37} \]

At \( T_e < 3000 \text{ K} \), these equations are valid, since only 6s electrons are excited and the heat capacity increases linearly with temperature. However, when the photon energy exceeds the ITT, d-band electrons are excited, causing a deviation in the chemical potential, \( \mu \), from the Sommerfeld Expansion for the free electron gas model [144]. It should be noted that the greater DOS associated with the d-band results in a greater absorption strength when the ITT is exceeded, as per Fermi's Golden rule [34]. Therefore with d-band excitation, electrons reach substantially higher temperatures due to the substantially higher electronic heat capacity of d-band electrons compared to s-band electrons. In this scenario, the accurate evaluation of the electronic heat capacity must include the consideration of the DOS and the number of electrons by determining how the chemical potential varies with temperature.

The electron temperature also impacts on the coupling rate of the energy from the electronic system to the lattice system. The coupling of energy between the electrons and lattice is described by the electron-phonon coupling factor, \( G_{ep} \), whilst the inverse of \( G_{ep} \) relates to the electron-phonon coupling rate. When the ITT is not exceeded, \( T_e \) is relatively low, and the temperature gradient between the electrons and lattice is relatively gradual. In this regime, the electron-phonon coupling factor, \( G_{ep} \), remains effectively constant \((2.8 \times 10^{16} \text{ W m}^{-3} \text{ K})\). However, when the ITT is exceeded, \( T_e \) is relatively high and the temperature gradient between the electrons and lattice is much steeper. This results in a more efficient coupling, which is reflected in a substantial increase in \( G_{ep} \). During electron-phonon coupling, only electrons within the energy interval \((k_B T_e)\) of the chemical potential can contribute, due to Pauli’s principle [138]. Therefore as \( T_e \) rises,
more electrons can couple to the phonons (larger $k_B T_e$) and $G_{ep}$ consequently increases.

In this study, the three laser wavelengths applied, UV, Green and IR have photon energies of 3.62 eV, 2.41 eV and 1.21 eV, respectively. Therefore, the UV and Green laser wavelengths have sufficient photon energy to exceed the ITT (1.8 - 2.4 eV) with a single photon, whereas the IR wavelength does not. Therefore at UV and Green wavelengths, the electronic temperatures and heat capacities reach substantially higher than those at IR wavelength. Consequently, the electron-phonon coupling time is far shorter following UV or Green ablation compared to at IR. For example, Lin and Zhigilei showed that the excitation of d-band electrons in Au resulted in a substantial increase in $T_e$, and consequently an order of magnitude increase in $G_{ep}$. It is proposed that the wavelength dependence of the Grain-Nanoparticle relationship observed in this study is as a consequence of differing absorption mechanisms for different photon energies and consequently different ablation mechanisms.

### 5.6 Ablation Mechanisms

The influence of the photon energy on the electronic response of Au subsequently impacts on the lattice heating and on the ablation mechanism that ensues. The excitation of d-band electrons at UV and Green laser wavelengths, but not at IR, results in higher $T_e$, $C_e$ and $G_{ep}$ that results in faster lattice heating than at IR laser wavelength.

The existence of the same Grain-Nanoparticle relationship at UV and Green laser wavelengths, but not at IR, implies that one ablation mechanism ensues at UV and Green and another ensues at IR. Possible mechanisms for ablation and nanoparticle generation are discussed at length in the literature, with support from computational models and experimental evidence. Nevertheless, the details of ablation mechanisms and nanoparticle formation are still unclear. This section explores the likely mechanisms occurring at the different laser wavelengths based on the results generated in this Chapter.
5.6.1 Laser Ablation at IR Wavelength

The lack of relationship between the grain microstructure of the Au film and the nanoparticles that were generated at IR laser wavelength, as shown in Figure 53b, suggests a photophysical ablation mechanism. A phase change of the film prior to nanoparticle formation would remove the grain boundaries thus preventing any relationship between the grains and the nanoparticles persisting. Such a phase change could be vaporisation or melting of the film.

The material response can be determined by the time for lattice heating and the lattice temperature, which can be explored using computational evidence. IR photons have insufficient energy to achieve significant d-band excitation in Au. Therefore, absorption of IR photons occurs predominantly by intra-band absorption by the $6s^1$ free carriers. As a result, $T_e$ and $C_e$ are low and thus $G_{ep}$ is appropriately represented by the ‘constant’ value of $2.8 \times 10^{16}$ W m$^{-3}$ K$^{-1}$ [48]. This results in a relatively long electron-phonon coupling time and thus slow lattice heating. This eliminates the possibility of stress build up in the film and thereby eliminates the mechanical fracture as an ablation mechanism [145]. These long time scales, on which electron-phonon coupling occurs following IR laser absorption, is likely to result in a phase change that eliminates the grain boundaries before ablation ensues.

The phase change that ensues could be either melting or vaporisation. In Section 4.5, it was determined that the energy volume density for the Au films exceeded the latent heat of melting but not the latent heat of vaporisation. The melting of the Au film can then result in the homogeneous or heterogeneous nucleation of liquid regions in the Au film, which can compete over extended periods. Homogeneous nucleation or phase explosion occurs when the film becomes superheated and rapidly decomposes to form liquid droplets. The formation and growth of these droplets to give nanoparticles typically follows the classical nucleation theory [145].

The broad range of nanoparticle sizes observed in Figure 53b could be attributable to multiple collisions within the plume, which can occur when material is ejected in different directions and with different kinetic energies and
is also influenced by the ambient conditions [59, 77]. This is conducive with the relatively slow heating of material and consequent ejection of material over an extended period. The competition between heterogeneous and homogenous nucleation can result in multiple liquid regions that are ejected and grow at different times. Homogeneous nucleation can occur on the time scale of several tens of picoseconds, whereas heterogeneous nucleation can occur over several hundred picoseconds [145]. It is therefore indicative of phase explosion to result in the ejection liquid clusters and droplets in a range of sizes.

5.6.2 Thermoelastic Ablation at UV and Green Wavelengths

The existence of the same linear Grain-Nanoparticle relationship following UV and Green laser ablation implies that the same ablation mechanism ensues at these wavelengths.

The d-band excitation following the absorption of UV and Green laser photons results in high $T_e$, and consequently an increase in the electron-phonon coupling rate by an order of magnitude [48]. The efficient transfer of energy from the very hot electrons to the relatively cold lattice occurs on such short timescales (~1 ps) that it has been shown to result in a build up of thermoelastic stresses in the material. If the time for laser heating is shorter than the time for mechanical relaxation (volume expansion), the heating occurs under a near constant volume condition [145]. In this case, compressive stresses are generated that interact with the surfaces of the film/substrate interface and result in tensile stresses that can cause mechanical fracture of the material. For Au, the time for mechanical relaxation is ~5 ps and therefore following UV and Green laser absorption, there is an increase in thermoelastic stress in the films.

The thermoelastic stress generated in the film during UV and Green laser ablation induces the breakup of the film. Localized lattice distortions, such as grain boundaries will reduce the stability of the Au crystal structure and therefore function as points of weakness or voids, from which the film breakup can originate [146]. The speed at which UV and Green laser ablation occurs, results
in an ablation mechanism that retains a relationship between the grain structure and the nanoparticles that are generated.

As the size of the grain increases, the wavelength dependent ablation mechanisms were unaffected. This further substantiates the claim that inter-band absorption is a dominant factor, as the corresponding absorption cross-section does not alter appreciably with grain diameter as the inter-band absorption is related to the electronic excitation of an Au atom, unlike many other material properties [147].

5.6.3 Phase Changes

The existence of the Grain-Nanoparticle relationship determined that no phase change of the film must ensue before nanoparticle formation, since the size relationship would be lost. However, phase changes can proceed following the thermoelastic break up of the film into grains. This is supported by the computational evidence that rapid lattice heating occurs prior to mechanical relaxation following d-band excitation [48]. However, after the initial fragmentation of the film into the grains, the high lattice temperatures reached would likely result in a phase change. Given the existence of the grain-nanoparticle relationship, vaporisation of the grains at this stage would not be possible, since this relationship would be lost. Therefore the grains are likely to melt following fragmentation. The melting temperature of bulk Au is 1336 K and the latent heat of melting is 2.86 kJ cm$^{-3}$ [134, 148]. The vaporisation temperature of bulk Au is 2873 K and the latent heat of vaporisation is 9.25 kJ cm$^{-3}$ [134, 148]. It was determined in Chapter 4 that the energy density exceeded the latent heat of melting but did not exceed the latent heat of vaporisation at $\phi_A$.

Figure 55 was produced by Chowdhury and it illustrates the surface lattice temperature calculated for Au following a 100 fs laser pulse for different laser fluences [149]. The absorbed laser fluence for each Au film was 0.3 J cm$^{-2}$, which, according to Figure 55, results in a peak surface lattice temperature of approximately 2800 K. This implies that the vaporisation temperature for Au is
not reached following the absorption of this fluence. The peak temperature was reached at 58 ps following the pulse, which also supports the long delay between mechanical fragmentation 1-5 ps, and the phase change of the material.

![Figure 55](image)

**Figure 55:** Figure extracted from article by Chowdhury et al. [149] to illustrate the surface lattice temperature of Au following a 100 fs laser pulse at four different absorbed laser fluences.

The temperature of the ejected nanoparticles has also been determined by Amoruso from the optical emission by Au nanoparticles in the plume [104]. The temperature was determined as 2110 K for the Au plume of nanoparticles, which also does not exceed the vaporisation temperature of Au.

The SEM images shown in Figure 47 and Figure 48 of the laser generated nanoparticles showed that they were largely spherical in shape. This supports the premise that the nanoparticles must be in a molten/liquid phase prior to their deposition. Liquid droplets will tend towards a spherical shape due to the LaPlace law, in order to minimise the surface tension, \( \gamma \), of the liquid.

\[
\gamma = \frac{\Delta p}{2H}
\]

where \( \Delta p \) is the pressure difference across the droplet/air interface and \( H \) is the curvature of the droplet.

When the temperature of the material exceeds the melting temperature, the molten particles will cool primarily via radiation to the surroundings. The
Stephan-Boltzmann equation can be combined with the emissivity value of a material, $\varepsilon$, to determine the amount of radiation emitted, $J$, per unit time:

$$\frac{dJ}{dt} = \varepsilon \sigma_s A T^4$$

Equation 39

where $\sigma_s$ is Stephan’s constant $5.6703 \times 10^8$ W m$^{-2}$K$^{-4}$ and $A$ is the surface area of the droplet. From thermodynamics, the heat capacity rate, $C$, describes the quantity of energy that a body can absorb or release per unit temperature, per unit time.

$$C = c_p \frac{dm}{dt}$$

Equation 40

where $c_p$ is the specific heat of the liquid and $dm/dt$ is the mass flow rate of the liquid.

The amount of radiation emitted by a particle is also dependent on its mass, $m$, the specific heat capacity, $c_p$, and the rate of change in temperature, $\Delta T$.

$$J = mc_p \Delta T$$

Equation 41

The equations can be combined and integrated over time and temperature to give Equation 42, in which the cooling time, $t_{cooling}$, from one temperature, $T_{hot}$, to another, $T_{final}$, can be determined for particles of different sizes.

$$t_{cooling} = \frac{Nk_B}{2\varepsilon \sigma_s A} \left[ \frac{1}{T_{final}^3} - \frac{1}{T_{hot}^3} \right]$$

Equation 42

The emissivity, $\varepsilon$, of Au (0.03) is relatively low compared to other metals and there the time for a ‘hot’ particle to cool below the melting temperature (1333 K) and re-solidify will be long. Figure 56 shows the calculated time required for particles with different radii to cool below the melting temperature (1333 K) starting from 2500 K. The re-solidification time for a nanoparticle (5 – 55 nm in radius) lasts for 0.3 – 3.5 ms, which gives sufficient time for the coalescence or breakup of the droplets.
In this study, the nanoparticles that were measured, had re-deposited onto the substrate. The distance over which the nanoparticles must travel to allow for re-solidification before re-deposition can be calculated from the cooling times in Figure 56 and the velocity of nanoparticle propagation during femtosecond laser ablation of metals, which has been measured as approximately 100 m/s [77]. This equates to a distance of 8 cm for a nanoparticle with a diameter of 29 nm.

5.6.4 Grain Breakup

Following the absorption of either UV or Green laser pulses, the film initially fragments into the individual grains. However, the linear Grain-Nanoparticle relationship in Figure 53a implies that for each average-sized grain, approximately seven average-sized nanoparticles result. Therefore, following the thermo-elastic breakup of the film into grains, further break up of the grains into smaller nanoparticles must ensue. It should again be emphasised that the method of collection introduces some bias into the number and size range of nanoparticles collected. The key result is not the number of nanoparticles that form, but that further break up of the grains must occur.

Several mechanisms were considered to explain the apparent break up of the grains into nanoparticles including jet formation[150], Rayleigh
Instabilities[151] and decomposition of a rapidly expanding liquid [152]. Such mechanisms drive the breakup of liquids into uniformly sized droplets and are driven by surface tension. Considering the hydrodynamic motion of ablation mechanisms such as Rayleigh instability and jet formation, it was determined that the melting process would occur prior to nanoparticle formation and would result in the loss of grain boundaries. Therefore the mechanism considered for further investigation was the Rayleigh-Charge instability.

Rayleigh-Charge instabilities stem from the emission of electrons, resulting in the build up of residual positive charges. Surface tension maintains the grains/droplets as a sphere as long as it exceeds the Coulombic force generated by the charges. Below the Rayleigh radius, \( r_{\text{Rayleigh}} \), the Coulombic force becomes greater than the surface tension and can result in the ejection of charges or the breakup of the droplet [151]. Chapter 6 will investigate the electron and ion emission during laser ablation at different wavelengths in order to ascertain whether Rayleigh – Charge instabilities could drive the breakup of the grains.

5.7 Summary and Conclusions

The aim of this study was to contribute experimental data to the areas of laser absorption, ablation and nanoparticle generation. This Chapter probed the importance of the grain microstructure of thin films and the laser wavelength on these processes by examining the nanoparticle debris. The wavelength dependence of the grain-nanoparticle size relationship indicated differing absorption mechanisms and consequently differing ablation mechanisms. This important experimental result matched well with previous computational studies into the non-equilibrium effects of laser absorption of differing photon energies by Au.

Based on these results, experiments will be presented in Chapter 6 to further probe the wavelength dependence of the ablation mechanisms and nanoparticle generation. The electron and ion emission will be monitored using a time-of-flight setup to ascertain whether the number of electrons emitted could indicate
that the Rayleigh-Charge instabilities is the driving mechanism for the break up of the Au grains. Additionally, the ejection of the nanoparticles will be imaged in real-time using optical emission and shadowgraphy setups. Details of the temporal and spatial evolution of nanoparticles will contribute to the overall picture of the wavelength dependence of femtosecond laser ablation mechanisms of Au films.

The main results from this Chapter are summarised as follows:

- **The absorption of laser energy by the electronic system in a 20 nm Au film differs at 343 nm (UV) and 515 nm (Green) compared to at 1030 nm (IR) laser wavelengths.** Laser wavelengths in this study were 343 nm (3.62 eV), 515 nm (2.41 eV) and 1030 nm (1.21 eV). Photons with $\hbar \nu < 1.9$eV deliver insufficient energy to achieve d-band excitation and thereby only s-band electrons are excited in an intraband process. Photons with $\hbar \nu > 1.9$eV exceeds the interband transition threshold (ITT) for d-band excitation, resulting in relatively strong absorption.

- **The absorption of photons that exceed the ITT results in higher $T_e$ and consequently a low $G_{ep}$, compared to the absorption of photons that do not exceed the ITT.** According to Fermi’s Golden rule, the higher density of states associated with the d-band compared to the s-band results in a greater absorption strength and heat capacity when the ITT is exceeded. Therefore when the ITT is exceeded, higher $T_e$ is reached, which results in a greater temperature gradient between the electrons and lattice and therefore a lower $G_{ep}$.

163
• The same, linear relationship exists between the volume of the film grains and the volume of nanoparticles generated during UV and Green femtosecond laser ablation of Au thin films
The energy of UV and Green photons exceeds the ITT resulting in high $T_e$ and fast electron-phonon coupling. Fast coupling induces thermoelastic stress, which culminates in the break up of the film into the grains, thus retaining a relationship between the grain size and the nanoparticle size.

• No Grain-Nanoparticle volume relationship was observed for laser ablation at IR wavelengths
The energy of IR photons delivers insufficient energy to achieve d-band absorption and hence relatively lower $T_e$ is reached and electron-phonon coupling occurs over a relatively longer time-scale. The longer time-scales result in a melting that eliminates the grain boundaries before the onset of nanoparticle formation. This thereby removes any possible relationship between the size of grains with the size of nanoparticles.

• The Grain-Nanoparticle relationship observed at UV and Green wavelengths showed that further fragmentation of the grain into smaller nanoparticles must occur after the initial thermoelastic ablation of the film.
The data showed that approximately seven average sized nanoparticles were sourced from each average sized grain. This number is biased by the collection method, the assumption of a columnar grain microstructure and subject to the standard deviations of grain and nanoparticle sizes. The data supports the concept that the grain fragments further, without vaporisation, thus retaining the grain-nanoparticle relationship. It is proposed that this fragmentation is potentially attributable to the rapid expansion of the liquid grains and the next Chapter investigates the Rayleigh-Charge contribution.
6.1 Introduction

The results in Chapter 5 indicated a wavelength dependence of the laser absorption and ablation mechanisms taking place in Au films. These differences were dependent on the energy of the photons interacting with the electronic system of Au. The absorption and ablation mechanisms differed when the photon energy was either above or below the interband transition threshold (ITT) for d-band electron excitation in Au (1.9 eV). The purpose of this chapter is to further probe this theory by monitoring the wavelength dependence of electron and ion emission from the Au films during laser ablation.

The results in Chapter 5 indicated that following the thermoelastic ablation of the Au film into the grains at UV and Green wavelengths, the grains broke up into smaller nanoparticles. This Chapter explores the possible contribution of Rayleigh charge instabilities to the fragmentation of the grains, by measuring the emission of charges during laser ablation. The absorption of a laser pulse by a material can result in the ejection of electrons, which results in unshielded
positive charges residing in the surface of the material. This positive charge can be offset by the emission of positive ions or on very short time-scales, the material can fragment due to Coulombic repulsion [153, 154]. A voltage biased Langmuir probe was set up within a vacuum chamber to measure the emission of both electrons and positive ions from a 20 nm thick Au film on Quartz during laser ablation at the same absorbed fluence for three different wavelengths.

From the data collected, it was possible to ascertain the number of electrons and ions ejected, the temporal profile of detection and the mechanisms for electron ejection. Finally, the combination of the number of electrons and ions detected is used to predict the net positive charge build up in the Au grains following ablation at each laser wavelength. This build up of charge is then discussed in terms of Rayleigh Charge instabilities in the grains and whether this culminates in their Coulombic fission into smaller nanoparticles.

To further explore the wavelength dependent ablation mechanisms and material ejection, a schlieren imaging setup was developed to achieve real-time visualisation of the nanoparticle plume during laser ablation. The temporal and spatial evolution of the nanoparticle plume was captured for the laser ablation of a 90 nm thick Au film at the three laser wavelengths to give further insight into the fundamental wavelength dependence of laser ablation of Au.
The objectives of this chapter are the following:

- Determine whether there is a wavelength dependence of the emission of electrons from a 20 nm thick Au film following the absorption of the same laser fluences. In particular determine ejection mechanisms and number of electrons emitted.

- Determine whether there is a wavelength dependence of the emission of positive ions from a 20 nm thick Au film following the absorption of the same laser fluences and compare to the electronic emission in terms of temporal evolution and number of species ejected.

- Ascertained whether the emission of electrons from the Au films is sufficient to generate Rayleigh Charge Instabilities in the grains which could contribute to the fragmentation of grains into smaller nanoparticles following UV or Green thermoelastic ablation.

- Develop a schlieren imaging setup to achieve real-time visualisation of the nanoparticle plume during laser ablation of thin Au films and to discern any differences in material ejection due to laser wavelength.
6.2 Electron Emission

This section explores the wavelength dependence of electron emission from an Au film during femtosecond laser ablation. The electrons were detected using a Langmuir probe under vacuum conditions. The Langmuir probe setup was first introduced in Section 3.5.1 and the key details are included again in this section. A single 20 nm thick Au film was selected for the electron and ion emission study and its properties are discussed in this section. Finally the wavelength dependence of the electron emission is presented in terms of the current-time waveforms produced on an oscilloscope following the impingement of charges on the Langmuir probe.

6.2.1 Electron Emission during Laser Ablation

To simplify the investigation into the wavelength dependence of electron and ion emission from thin Au films, a single 20 nm Au film was selected for all Langmuir probe experiments. The 20 nm Au film was sputter deposited onto a Quartz substrate. The reflectance of this film was measured as 39%, 50% and 87% and the transmittance was calculated as 26%, 27% and 2% for UV, Green and IR laser wavelengths, respectively. Therefore at UV, Green and IR wavelengths, 35%, 23% and 11% of the applied laser fluence was absorbed. These values assume that the laser energy is absorbed entirely by the film and not by the substrate. A range of laser fluences were applied to the film at each laser wavelength to give an absorbed fluence range between 50 – 800 mJ cm\(^{-2}\). The absorbed fluence range relates to applied laser fluences at UV, Green and IR wavelengths of 0.14 – 2.29 J cm\(^{-2}\), 0.21 – 3.47 J cm\(^{-2}\) and 0.45 – 7.27 J cm\(^{-2}\), respectively. The \(\phi_{\text{th}}\) at UV, Green and IR wavelengths were calculated as 0.11 J cm\(^{-2}\), 0.16 J cm\(^{-2}\) and 0.35 J cm\(^{-2}\), respectively, which equated to \(\phi_A\) of 0.04 J cm\(^{-2}\) for all wavelengths.
To monitor the emission of electrons from the Au film, a Langmuir probe was orientated perpendicular to the Au film at a distance of 30 mm above the surface during laser ablation under vacuum conditions (10^{-6} Torr). A single femtosecond laser pulse was absorbed by the Au film and electrons were detected normal to the surface. The Langmuir probe was biased with a positive voltage (+30 V) and impinging charges on the probe generated a current that was measured using an oscilloscope. The current generated due to the electrons were measured over time and was compared at the three laser wavelengths (for the same absorbed fluence).

6.2.2 Wavelength Dependence of Electron Emission

This section presents the current-time waveforms measured using a positively biased (+30V) Langmuir probe during femtosecond laser ablation at UV, Green and IR laser wavelengths. The applied laser fluence was adjusted depending on the optical properties measured in Chapter 4 to give comparable absorbed laser fluences at each laser wavelength. The impingement of electrons on the probe resulted in negative voltage-time waveforms, from which the absolute current-time waveforms are presented for different absorbed fluences at UV, Green and IR wavelengths in Figure 57.

Figure 57: Current-time (absolute) waveforms detected with positively biased probe at different absorbed laser fluences (J cm^{-2}) for laser wavelengths (a) UV (b) Green and (c) IR. Note different scale in (c). t = 0 relates to the time that the laser pulse is first incident on the target Au surface, as determined using a photodiode.
The key observations from Figure 57 are given in the list below, each of which, will be discussed in more detail in later sections:

1) The measured current increased with absorbed fluence at all wavelengths.
2) The current generated from electron emission is significantly higher following UV or Green laser pulses, compared to following an IR laser pulse.
3) The detection of electron emission occurs over longer periods following a UV or Green laser pulse, compared to an IR laser pulse.
4) There are at least two distinguishable peaks in the waveforms following UV and Green laser ablation, whereas only one was observed at IR wavelength.

The presence of different peaks in the current-time waveforms (Figure 57) indicates that there were potentially different emission mechanisms for the electrons over time. The two dominant mechanisms discussed for electron emission in the literature are photoelectric emission and thermionic emission, which were introduced in Section 2.5.1. In the next two sections, the ejection mechanisms for the electrons associated with the two distinct peaks observed in Figure 57 are explored.

To ascertain the number of the electrons emitted via each mechanism, a Gaussian-Lorentzian curve was fitted to each peak; A curve was fitted to the first peak, with the peak matching that of the peak in the waveform. A curve was then fitted to the second peak with the integration ranging from the rise of the peak on the left hand side.

6.3 Multiphoton Photoemission (MPPE) of Electrons

This section explores the Multiphoton Photoemission (MPPE) mechanism. Electrons can undergo photoemission if they absorb sufficient energy to overcome the work function of Au (4.8 - 5.1 eV). If the energy of a single photon
is insufficient, multiple photons can be absorbed in a process called multiphoton photoemission (MPPE). Importantly, this mechanism can only take place during the laser pulse duration. This section analyses the data relating to the first peak in the current-time waveforms (Figure 57) and presents the evidence for the MPPE mechanism as the source of these electrons.

6.3.1 MPPE Electron Yield

The first peak observed in each of the current-time waveforms (Figure 57) related to the electrons arriving at the probe first and was observed for all three laser wavelengths. Each peak was fitted with a Gaussian / Lorentzian mix curve and the number of electrons contributing to each peak was ascertained by integration using Equation 34. At all wavelengths this first peak was fitted with a predominantly Gaussian curve. The number of electrons contributing to the first peak is shown at a range of absorbed fluences for the three wavelengths in Figure 58.

![Figure 58: Comparison of the number of electrons emitted at comparable absorbed fluences and different laser wavelengths that contributed to the first peak.](image)

Firstly, Figure 58 shows that the number of electrons detected increases with absorbed fluence at all three wavelengths. Secondly, the number of electrons emitted increases following a laser pulse of IR, Green and then UV wavelengths. Since the quantity of material removed is largely limited by the film thickness and beam diameter, this increasing number of electrons are being ejected from
the same quantity of removed material each time.

These observations can be understood by considering the electronic response to photon absorption. For electron emission to ensue, sufficient photon energy must be absorbed by the electron to overcome the work function of the material. If a single photon has insufficient energy for an electron to overcome the work function, multiple photons can be absorbed in a process called multiphoton photoemission (MPPE). The rate of MPPE emission, $J_n$, is described by Equation 43 and is dependent on the laser intensity, $I$, and the number of photons required, $n$.

$$J_n = \sigma^{(n)}(\lambda) I^n$$

Equation 43

The likelihood of MPPE is characterised by the multiphoton absorption cross-section, $\sigma^{(n)}(\lambda)$. This cross-section, $\sigma_n$, is dependent on the number of photons required to be absorbed by an electron for it to exceed the work function of the material.

The photon energy associated with the UV, Green and IR wavelengths were 3.62 eV, 2.41 eV and 1.21 eV, respectively. Assuming a work function of 4.8 eV for Au, the number of photons required for MPPE to ensue, $n$, would be 2, 2 and 4 photons at UV, Green and IR wavelengths, respectively. Figure 58 showed that the electron current was significantly lower following IR ablation compared to UV or Green ablation. This is a reflection of the lower probability of MPPE with IR photons, since the $\sigma_n$ decreases as $n$ increases.

Since $J_n$ is proportional to $\sigma_n I^n$, the rate of MPPE increases exponentially with laser intensity, however, the absorption cross-section for increasing $n$ will reduce this effect. At very high laser intensities there will be sufficient incident photons to overcome the small $\sigma_n$ where high $n$ is required. This explains why electrons were not detected at low fluences at IR wavelengths, as $\sigma_n$ was too small and the number of incident photons too few. However, at higher fluences, a sufficient number of IR photons were incident to overcome the small $\sigma$ and achieve MPPE of electrons.

A curious observation Figure 58 was the crossover of the number of detected electrons at approximately 0.5 J cm$^{-2}$, whereby the number of electrons detected
following Green ablation surpassed the number of electrons detected following UV ablation. To explore the significance of this crossover point, the number of photons absorbed (instead of absorbed fluence) was considered for each wavelength. An absorbed fluence relates to a different number of absorbed photons at the three laser wavelengths. For example, a laser pulse of a certain fluence, will comprise of a greater number of IR photons than Green or than UV photons since the UV, Green and IR photons have energies of 3.62, 2.41 and 1.21 eV, respectively. To illustrate this point, Figure 59a presents the number of UV, Green or IR photons that contribute to make up a certain laser fluence. The Figure shows that the number of photons diverges for the three wavelengths with increasing laser fluence.

Given that the number of photons required to exceed the work function of Au is the same (n = 2) for both UV and Green photons, the greater number of photons absorbed at Green compared to UV may result in a greater number of electrons emitted. To explore this hypothesis, the number of photons absorbed was plotted against the number of MPPE electrons detected and is shown in Figure 59b.

![Figure 59](image)

**Figure 59:** (a) The number of UV, Green or IR photons that are required to achieve different fluences (b) the number of photons absorbed against the number of MPPE electrons detected at three laser wavelengths. Error bars representing the standard deviation of the number of electrons detected is provided for the data at the UV wavelength.

When the absorbed laser fluence (Figure 58) was replaced by the absorbed number of photons (Figure 59b), a significant difference was observed for the electrons detected following a UV or Green pulse, compared to the number of electrons detected following an IR pulse. Linear trendlines were fitted to the UV, Green and IR data in Figure 59b with $R^2$ values of 0.89, 0.91 and 0.62,
respectively. Error bars represent the standard deviation (1.7 x 10^8 electrons) associated with the UV wavelength observed for the number of electrons detected which acts as a representation for the data. Linear trendlines were fitted to the data in Figure 59b and the gradients were found to be approximately the same at UV (7.6 ± 1.7) and Green (8.2 ± 1.9) wavelengths but significantly lower at IR wavelength (2.0). The gradients showed that the rate of MPPE emission following a UV or Green laser pulse is approximately the same i.e. the same number of electrons are produced for a given number of photons absorbed, N_{photons}. When considering the MPPE mechanism this same efficiency is expected, since at both UV and Green wavelengths, two photons must be absorbed by an electron to overcome the work function of Au.

Despite having the same gradient, the UV and Green data in Figure 59b are offset from one another. This shows that the threshold N_{photons} for electron emission is greater for a Green pulse than for a UV pulse. The reason for this difference is attributable to the difference in σ_n, which varies with wavelength. Values of σ_n for two photon absorption (units of cm^4s) are difficult to establish since it represents a non-linear absorption process. However, the probability of absorbing two photons is partially dependent on the absorption cross-section (units of cm^2) of one photon. The absorption cross-section for one photon is proportional to the absorption coefficient, α, and inversely proportional to the atomic number density of the material. Since the atomic number density is the same at both wavelengths, the difference observed in Figure 59b is attributable to the difference in α at each wavelength. The values of α for UV and Green are 67.3 x 10^6 and 51.6 x 10^6 cm\(^{-1}\), respectively. Therefore the σ_n is lower at the Green wavelength than for the UV wavelength. However, once a threshold N_{photons} is exceeded for Green photons, this compensates for the smaller σ_n for Green photons compared to UV photons.

The number of electrons detected was significantly lower following the absorption of an IR laser pulse compared to either UV or Green pulses, as shown in Figure 59b. Additionally, a greater N_{photons} was required at IR wavelength to achieve electron emission. This is as a result of the lower energy associated with an IR photon, whereby n = 4 and the σ_n is consequently significantly smaller at the IR wavelength, compared to either UV or Green wavelengths.
6.3.2 MPPE Electron Emission Rate

Electrons can undergo MPPE if they absorb sufficient photon energy during the laser pulse to overcome the work function of Au (4.8 eV). Second order MPPE is possible at UV (3.62 eV) or Green (2.41 eV) wavelengths, whereas fourth order MPPE would be required at IR (1.21 eV) wavelengths. The yield of MPPE electrons, \( J_n \), for different numbers of absorbed photons, \( n \), is given by [73].

\[
J_n = \alpha_n A \left( \frac{e}{h \nu} \right)^n (1 - R)^n I^n T_{es}^{-2} F \left( \frac{n h \nu - W_F}{k_B T_{es}} \right)
\]

Equation 44

where \( \alpha_n \) is the absorption coefficient for the absorption of \( n \) photons, \( A \) is the Richardson’s coefficient described in Equation 15, \( W_F \) is the work function of the material, \( T_{es} \) is the temperature of the surface electrons and the function \( F(x) \) is the Fowler function expressed in full in Reference [155]. The electron emission yield, \( J_n \) is therefore proportional to \( I^n \), where \( I \) is the laser intensity and \( n \) is the number of photons absorbed in the MPPE process.

To determine whether the electrons contributing to the first peak in Figure 57 are emitted via the MPPE mechanism, Equation 44 can be simplified to give:

\[
\ln J = n \ln I
\]

Equation 45

whereby a graph of \( \ln I \) against the \( \ln J \) would give rise to a linear plot, where the gradient would provide the value of \( n \) for the MPPE mechanism at each wavelength. Figure 60 presents the logarithmic plots of the laser intensity absorbed against the MPPE electron yield, \( J \), as per Equation 45.
Figure 60: Logarithmic plot of peak laser intensity versus the electronic current generated for the first peak. Gradients indicate the dependence of the electron emission on the number of photons absorbed during MPPE.

The gradients of the linear trendlines for the data in Figure 60 relate to the number of photons absorbed, n, giving rise to the emission of electrons via MPPE. The plot produced values for n of 1.1, 2.6 and 3.8 for UV, Green and IR laser photons, respectively. The measured values matched well with the expected values of 1.3, 2.0 and 3.9 eV, assuming the work function of the material is 4.8 eV. However, quantum mechanics dictates that only integer values of photons are absorbed by an electron, with the remaining energy contributing to the internal and kinetic energy of the electron. Therefore the integer values of n would be 2, 2 and 4 for UV, Green and IR photons, respectively. The small deviations from these integer values could feasibly be accounted for by errors in the fit or integration under the peaks, or indeed contributions from other emission mechanisms during this period. However, the values determined indicate that the dominant mechanism for the emission of these electrons is MPPE. The fitting of this data further supports the hypothesis that the emission mechanism for the electrons associated with the first peak in Figure 57 was MPPE [156].
6.4 Thermionic Emission of Electrons

The previous section analysed the electron data associated with the first peak observed in the current-time waveforms of Figure 57. Analysis indicated that the electrons contributing to this first peak were emitted via MPPE. This section analyses the electron data associated with the second peak observed in Figure 57. Analysis has indicated that the electrons contributing to this second peak were emitted via thermionic emission.

Thermionic emission occurs when sufficient thermal energy induces charge carriers to overcome the work function of the material. This section presents evidence for the thermionic emission mechanism, the yield of electrons detected, and also applies the Richardson-Dushman equation for thermionic emission to determine the electron temperature of the emitted electrons. Most significantly, this section again shows the wavelength dependence of electron emission during laser ablation of Au.

To distinguish whether the electrons contributing to the second peak were also emitted by the MPPE mechanism, the electron data was analysed using the same method shown in the previous section (Figure 60). A plot of LnI versus LnJ yielded no relationship at each wavelength. This implied that these electrons were emitted via an alternative mechanism.

The shape of the waveforms (Figure 57) also contributes information regarding the mechanisms of electron emission. The first peak is sharp and occurs over a short period, since the MPPE of electrons must occur during the pulse duration. Contrarily the second peak is shown at a later time and has an initial sharp rise followed by a slow decay over several microseconds. This is conducive to the thermionic emission mechanism since the rate is partially dependent on the electron $T_e^2$. The absorption of laser energy causes a steep rise in $T_e$, which then decays over time due to electron-phonon coupling with the relatively cold lattice. Additionally, thermionic emission results in a decrease in the electron temperature, which reduces the thermionic rate and the electron-phonon coupling efficiency. This sharp temperature rise and slow decay results in a high
thermionic emission rate followed by a slow decay, which mirrors the shape of the waveform for the second peak.

The second peak was only observed following a UV or Green laser pulse, but not following an IR pulse. This wavelength dependency can again be interpreted in terms of the partial $T_e^2$ dependency of thermionic emission. It was deduced in Chapter 5 that since the IR photons do not exceed the ITT of Au, the absorption ensues via the 6s electrons. However, the absorption of UV or Green photons exceeds the ITT and thus can also excite the 5d electrons to the Fermi level, which consequently results in electrons with substantially higher temperatures, $T_e$. Since the electrons reach higher temperatures following UV or Green photon absorption compared to IR, the electrons are more likely to overcome the work function of Au and result in thermionic emission.

The electron data associated with the second peak (Figure 57) is analysed in the following two sections. Firstly, the electron yield associated with the second peak is calculated and the wavelength dependence of the mechanism is explored. Then the data is processed in terms of the Richardson-Dushman equation for thermionic emission, which provides information on the emission rate and electron temperature.

6.4.1 Thermionic Emission Electron Yield

The number of electrons contributing to the second peak was calculated by integrating under the fitted curve as per Equation 34 and the results are shown in Figure 61. The fitted curve was predominantly Lorentzian, which suggests a dampening component to the detected electron density that was not observed for the primary photoemission peak, which was predominantly Gaussian.
Figure 61: Number of electrons detected following thermionic emission at different absorbed laser fluences with UV or Green wavelength.

Figure 61 showed that the number of electrons emitted via thermionic emission increased with absorbed fluence. An increase in the absorbed fluence equates to an increase in the number of incident photons, which can therefore excite more d-band electrons, shifting the chemical potential, thus overcoming the work function via thermionic emission.

The number of electrons emitted by MPPE (Figure 59) was compared to the number of electrons emitted by thermionic emission (Figure 61). The thermionic emission of electrons, following UV and Green laser ablation, occurred over substantially longer periods than for MPPE (microsecond relative to nanosecond time-scale). This resulted in approximately five times more electrons detected following thermionic emission than following MPPE. The MPPE mechanism can only occur during the lifetime of the laser pulse, after which thermionic emission can continue as long as the electrons remain at sufficiently high temperatures.

Figure 61 also showed that the number of electrons detected following a UV pulse is marginally greater than the number detected following a Green pulse. Interestingly, there was an absorbed laser fluence (0.52 J cm$^{-2}$), above which the number of electrons detected following a Green laser pulse exceeded the number produced at UV. A crossover of the Green and UV data was also observed for the MPPE data (0.5 J cm$^{-2}$) for the plot of absorbed fluence against number of electrons detected. To ascertain whether this crossover was as a result of the greater number of Green photons absorbed compared to UV photons, for a given
fluence, the absorbed number of photons was plotted against the number of electrons detected and is shown in Figure 62.

![Graph of absorbed number of photons against the number of electrons detected following thermionic emission.](image)

**Figure 62:** Graph of absorbed number of photons against the number of electrons detected following thermionic emission.

Figure 62 shows that the linear trendlines associated with the number of thermionic electrons detected for a given absorbed number of photons at UV and Green wavelengths, with $R^2$ values of 0.94 and 0.78, respectively. The gradients of the trendlines at UV $(46.7 \pm 7.7)$ and Green $(48.2 \pm 6.3)$ wavelengths were statistically similar and therefore indicated that the thermionic emission rate (i.e. number of electrons emitted per photon absorbed) is effectively the same for both UV and Green wavelengths. This data indicates the importance of the ITT for d-band excitation. The absorption of a single UV or Green photon by Au can result in the excitation of 5d electrons to the Fermi level, thus shifting the chemical potential associated with the Fermi-Dirac electron distribution. This shift in chemical potential results in electrons with high temperatures that can overcome the work function of Au. The same emission rate of thermionic electrons for both UV and Green photons indicates the same electronic response to the absorption of the incident laser pulse. Significantly, the IR photons provide insufficient energy to exceed the ITT and the data collected showed no evidence of thermionically emitted electrons following IR absorption.

Despite the thermionic emission rate per absorbed photon being the same for UV or Green wavelengths, a higher threshold number of photons were absorbed before the onset of thermionic emission at Green compared to UV. The
wavelength dependence of thermionic emission will be discussed in the next section with regard to the Richardson-Dushman thermionic emission rate equation.

6.4.2 Thermionic Electron Emission Rate

The emission flux, $J_T$, for thermionic emission is given by Richardson-Dushman equation [157]:

$$ J_T = A T_e^2 e^{-\frac{W_F}{k_B T}} $$

Equation 46

where $A$ is the Richardson constant ($1.2 \times 10^6$ amp m$^{-2}$ K$^2$) [158]. The equation can be used to ascertain the temperature of the electrons emitted by thermionic emission from the emission rate, $J_T$. Values of $J_T$ (electrons m$^{-2}$ s$^{-1}$) were estimated for a range of surface electron temperatures, $T_e$. The number of electrons was then deduced from $J_T$ by considering the dimensions of the Langmuir probe ($1.13 \times 10^{-6}$ m$^2$) and the time period of thermionic emission (3.5 µs). A plot of the expected electron temperature against the number of detected electrons at the Langmuir probe is shown in Figure 63a. This data was then used to estimate the electron temperature based on the number of thermionic electrons detected (Figure 61). Figure 63b shows how the electron temperature varied with the absorbed laser fluence and wavelength.

![Figure 63](image-url)

(a) Calculated number of thermionic electrons emitted from Au as a function of the surface electron temperature as determined from Richardson-Dushman equation. (b) Estimated electron temperature as a function of absorbed laser fluence based on the data in Figure 61 and the Richardson-Dushman equation. Lattice properties of melting and vaporisation (vap) temperatures (temp) are indicated.
Figure 63b shows that the temperatures of the detected electrons were approximately 2500 K and only increased by 300 K for the range of absorbed laser fluences used in this study. Figure 63b also shows that the electron temperatures reached following both UV and Green laser ablation were within 100 K of one another over the absorbed fluence range. Since there was an insufficient number of thermionically emitted electrons detected at the IR wavelength, it is assumed that the electron temperatures reached were significantly lower. This result again supports the hypothesis that following UV or Green laser ablation, d–band excitation is achieved and results in higher electrons temperatures. This consequently results in a greater thermionic emission rate and a greater number of detected electrons at UV or Green wavelengths compared to that observed at the IR laser wavelength.

A notable observation from Figure 63b, was that the electrons reached temperatures around 2500 K, but did not exceed the vaporisation temperature of Au. Since the lattice temperature is dependent on the coupling of energy from electrons, this data further supports the calculations shown in Chapter 4, that during laser ablation in this fluence region, the vaporisation temperature is not exceeded.

### 6.5 Positive Ion Emission

This section presents data of the detection of positive ion emission from an Au film during laser ablation. The Langmuir probe setup was used to determine whether the positive ion component exhibited a wavelength dependence as with the electron emission. The detection of the ionic component would also indicate whether the electron current was drawn directly from the film or from a plasma
6.5.1 Wavelength Dependence of Positive Ion Emission

Current-time waveforms were collected using a negatively biased (-30V) Langmuir probe at UV, Green and IR laser wavelengths at comparable absorbed fluences. The impingement of positive ions on the probe resulted in single peaked positive voltage-time waveforms at all wavelengths. The currents produced were lower by an order of magnitude than those generated by the impinging electrons. The area under the curve-fitted waveforms were integrated to determine the number of ions produced per pulse using the same method as for the electrons. The number of positive charges detected per pulse are shown in Figure 64a for a range of absorbed fluences and three laser wavelengths. The data was also plotted for the number of absorbed photons against the number of positive charges detected per pulse and is shown in Figure 64b.

![Figure 64](image)

Figure 64: (a) Absorbed laser fluence against number of ions detected by the Langmuir probe following the absorption of increasing fluence by a 20 nm thin Au film at three laser wavelengths. (b) Number of absorbed photons against number of ions detected.

Firstly, Figure 64a shows that the current generated from positive ion emission increased with absorbed laser fluence at all wavelengths. It has previously been determined that there is a logarithmic relationship between the ion yield and the laser fluence [156], although here, and in another study [159], a linear relationship was determined. The increasing fluence absorbed drives the emission of electrons, which results in an increasing build up of positive charge, which can be partially reduced through the ejection of ions. Therefore, the
increase in electrons emitted with fluence, drives the increase of ions emitted with fluence observed in Figure 64b.

Secondly, positive ions were detected at significantly lower fluences following UV or Green laser pulses, compared to an IR laser pulse. This factor is again driven by the relative number of electrons emitted at these wavelengths. Additionally, the current generated from impinging ions is strongly dependent on the electron temperature [5], which is substantially higher at UV and Green than at IR due to d-band excitation.

As was the case for electron emission, there was a crossover of the number of ions emitted at UV and Green laser wavelengths with absorbed laser fluence (Figure 64a). The crossover fluence was approximately 0.32 J cm\(^{-2}\), which was lower than the 0.5 J cm\(^{-2}\) for electron emission. The plot of the absorbed number of photons against the number of positive ions detected (Figure 64b) showed that the number of ions emitted per photons absorbed was similar for all wavelengths, but the threshold number of photons was significantly higher for IR photons compared to UV or Green photons. Figure 64b also indicates that when a low number of photons are absorbed (< 1.5 \times 10^{13}) there is a difference in the emission of ions at UV or Green wavelengths. However, when a higher number of photons are absorbed (> 1.5 \times 10^{13}), the emission of ions becomes less dependent on the photon energy.

### 6.5.2 Temporal Profile of Emissions

To understand the temporal profile of plasma emission, the electron and positive ion emission were compared at an absorbed fluence of 0.3 J cm\(^{-2}\), which related to the \(\phi_{NP}\) used throughout Chapter 5. The applied laser fluences at UV, Green and IR wavelengths were 0.78, 1.46 and 2.07 J cm\(^{-2}\), respectively. Figure 66 presents the electron emission (negative) and positive ion emission (positive) generated following the absorption of 0.3 J cm\(^{-2}\) at UV and Green laser wavelengths. Note that the positive current has been magnified by a factor of 10.
Figure 65: Temporal profile of the current generated by positive and negative emissions following the absorption of a 0.3 J cm\(^{-2}\) laser pulse at (a) UV and (b) Green laser wavelengths. Electron emission was measured with a voltage bias of +30V and positive emission was measured with a voltage bias of -30V. Note: the positive emission has been multiplied by 10.

The same comparison of positive and negative emissions at 0.3 J cm\(^{-2}\) is presented for the IR laser wavelength in Figure 66. Note the difference in scale on the y-axis compared to the previous Figure.

![Figure 66](image_url)

Figure 66: Temporal profile of the negative and positive emissions detected following the absorption of 0.3 J cm\(^{-2}\) at IR laser wavelength.

Figure 65 shows that the positive ions arrive at the probe simultaneously with the MPPE electrons (178 km s\(^{-1}\)). Since the electrons have a higher mobility and thermal velocity compared to the heavier positive ion component, this indicates that these electrons must be coupled with the ions as a plasma. This coupling resulted in lower kinetic energies of electrons (0.01-0.05 eV) and higher kinetic energies of the ions compared to other studies [160, 161]. However, the calculation of the kinetic energy of the charged species assumes that the charges are travelling unhindered from the target to the probe. The expansion of the hot
electronic component generates an electrostatic sheath above the target surface, which acts to accelerate the ions i.e. an electric field is formed. Equally, the electrostatic sheath acts to decelerate the electrons. This effect is known as the space-charge effect (Section 2.5.4).

Fast emission of ions can be indicative of Coulombic explosion, as opposed to thermal vaporisation [62]. This high kinetic energy of ions at UV and Green wavelengths could indicate a strong electric field generated by the large number of electrons emitted, that act to accelerate the ions away from the target. The magnitude of the electric field, \( E \), is dependent on the electron kinetic energy and the gradient of electron density along the normal, \( z \) [58].

\[
E = \frac{E_k(t)}{e} \frac{d \ln n_e}{dz}
\]

Equation 47

where \( E_k \) is the kinetic energy of the electrons, \( t \) is the time. If \( E \), is great enough, ions are accelerated.

Figure 65 also shows that the current generated from impinging ions is significantly lower than for the electrons by several orders of magnitude. Since the currents generated by the impinging electrons or ions is proportional to their respective number densities, this could be interpreted as a greater number of electrons are emitted from the Au grains, compared to the number of positive ions (assuming that the Au ions have a single positive charge [5]). It may also be due to the electrons and positive ions interacting differently with the probe.

The difference in the number of ions detected compared to electrons, implies that there is a significant unshielded positive charge unaccounted for. One hypothesis considers the thermoelastic ablation of the film into grains following either a UV or Green laser pulse, and proposes that the positive charge may reside in the surface of the grains. These positively charged particles travel at significantly slower velocities than the electrons or ions, but also are not detectable using a Langmuir probe due to the interaction of a particle with the probe.

This section once again highlights a wavelength dependence for the electron and ion emission from an Au film. Figure 65 showed strong similarities between the electron and ion emission at UV and Green wavelengths. Conversely, Figure 66
evidenced no positive ion emission at IR wavelength and a lower electron current compared to at either UV or Green wavelengths. The wavelength dependence of electron and ion emission has been discussed in previous sections with respect to d-band excitation.

6.5.3 Emission Threshold Fluences

In the previous sections, data was presented that showed the variation in the number of electrons and ions emitted from an Au film during laser ablation at different wavelengths and fluences. To determine the threshold absorbed fluence for plasma emission, linear trendlines were fitted to the graphs in Figure 58 (MPPE), Figure 61 (Thermionic) and Figure 64 (Ions). These trendlines were then extrapolated to \( y = 0 \), from which the threshold fluences for electron emission (MPPE and Thermionic) and positive ion emission were determined at each laser wavelength. These threshold fluences were then compared to the ablation threshold fluence, \( \phi_A \), for the Au film (0.04 J cm\(^{-2}\)) and the results are shown in Figure 67.

![Figure 67: Comparison of threshold fluences for ablation electron emission (MPPE and Thermionic) and positive ion emission at the three laser wavelengths.](image)

Figure 67 shows that the threshold fluence for all charge emissions increases from UV to Green to IR wavelength, due to their decreasing photon energy. The threshold fluence for MPPE electron emission was determined for UV, Green
and IR wavelengths as 0.028, 0.180 and 0.330 J cm$^{-2}$, respectively. The threshold fluence for thermionic emission was determined for only UV and Green wavelengths as 0.11 and 0.23 J cm$^{-2}$. No thermionic emission was detected at the IR wavelength. The threshold fluence for ion emission was determined for UV, Green and IR wavelengths as 0.029, 0.180 and 0.490 J / cm$^{-2}$, respectively.

Importantly, at UV and Green wavelengths, the value for the MPPE electron and ion emission threshold fluence is the same as each other. However, at the IR wavelength, the threshold fluence for ion emission was substantially higher than for MPPE emission. This indicates that at IR wavelengths, a plasma is not generated immediately following MPPE emission of electrons, and is only generated at a substantially higher fluence. At UV and Green wavelengths, the threshold fluences for MPPE electron and ion emission are the same, which indicates the presence of a plasma above this threshold.

Figure 67 also indicates how these threshold fluences for plasma generation compares to the ablation threshold of the film. At all laser wavelengths, the absorbed ablation threshold fluences were determined as 0.04 J cm$^{-2}$. All emission threshold fluences exceed the ablation threshold fluence, apart from the MPPE emission of electrons at the UV wavelength.

6.6 Charge Contribution to Laser Ablation

The purpose of this Chapter is to investigate the contribution of charge emission to the wavelength dependent ablation mechanisms of Au films and nanoparticle generation. In particular, following the thermoelastic ablation of the Au films during UV or Green laser ablation the mechanism of grain fragmentation into smaller nanoparticles remained unclear.

As a reminder, the key result of Chapter 5 was a linear relationship between the size of the grains of the Au film and the size of the nanoparticles at both UV and Green laser wavelengths, but not at IR. It was proposed that at photon energies in excess of ITT, high electron temperatures, fast electron-phonon coupling and thermoelastic ablation occurred, thus retaining a size relationship between the
grain and nanoparticles. For incident photons below the ITT, only intraband absorption was achievable via the 6s electrons and this resulted in relatively lower electron temperatures, slower electron-phonon coupling and a photothermal ablation mechanism. This was evidenced by the lack of size relationship between grains and nanoparticles at the 1030 nm laser wavelength.

The Grain-Nanoparticle size relationship (UV/Green wavelengths) indicated that following thermoelastic ablation (ps), the grains must fragment further to the final nanoparticles that were measured. By volume, the average sized nanoparticle was approximately seven times smaller than the average sized grain. It should also be noted that the collection method for the nanoparticles will induce some bias into the size of the measured nanoparticles, which would affect the exact number of nanoparticles each grain breaks up into. Additionally, the value of seven is based on the average values for nanoparticle and grain size.

Therefore the hypothesis is that if a sufficient number of electrons are ejected during laser ablation, this would result in unshielded positive charges residing in the grains. If sufficient positive charges are present in the grains, Rayleigh charge instabilities can result in the Coulombic fission of the grains into nanoparticles.

The ejection of electrons typically occurs from the surface of the metal, which leaves a highly unstable surface of positively charged Au ions that typically extends to nanometer thicknesses [62]. In order to replenish this charge deficit and restore charge neutrality, electrons must move from other parts of the material. However the resistivity of thin Au films has been shown to be an order of magnitude higher than that of bulk Au due to the confinement [2]. The positive ions are therefore unshielded for longer time periods compared to bulk materials. For this reason, the contribution of Rayleigh Charge instabilities are explored as a possible source of grain break up.

Firstly, the forces acting on the grains is discussed in the next section before introducing the additional Coulombic repulsion induced by the presence of unshielded positive charges. The data collected in this Chapter for electron and ion emission is used to predict the positive charge residing in the Au grains and whether this exceeds the Rayleigh charge stability limit. All calculations were
carried out using the data collected at an absorbed fluence of 0.3 J cm$^{-2}$ ($\phi_{NP}$) at the three laser wavelengths. This section is particularly focused on the forces acting on the grains following thermoelastic ablation at UV and Green laser wavelengths.

### 6.6.1 Forces Acting on Grains

Following the thermoelastic ablation of the film into the grains (ps) at UV and Green wavelengths, phase changes will occur on longer timescales (ns). Previous calculations (Figure 43 and Figure 63b) showed that the electron temperature exceeds the melting temperature of Au, but not the vaporisation temperature. Therefore as these ‘hot’ electrons couple to the lattice, the Au grain melts. Earlier calculations based on Au emissivity (Figure 56) showed that Au droplets can remain in the molten state for several milliseconds before cooling and resolidifying. Therefore throughout this section, calculations are made based on the assumption that once the grains have fragmented, they melt. This was supported by SEM evidence in Chapter 4, where the imaged nanoparticles were spherical, since the minimum surface free energy configuration for a molten droplet is a sphere. Therefore all calculations in this section assume that the grains are spherical molten droplets.

According to the Young-Laplace equation, for a droplet to be stable, the forces acting inwards on the droplet, $F_{in}$, must balance the force acting outwards on the droplet, $F_{out}$.

$$
\Delta P \pi r^2 = \gamma \pi r^2
$$

Equation 48

where $r$ is the radius of the droplet, $\gamma$ is the surface free energy and $\Delta P$ is the difference in the internal and external pressure of a droplet. Surface free energy, $\gamma$, describes the quantity of free energy required to increase the surface by one unit area. In the case of liquids, the surface free energy (J m$^{-2}$) is numerically equal to the surface tension, $\sigma$ (N m$^{-1}$). The surface tension is dependent on the intermolecular separation length and the molecular binding
energy. The surface tension is a force that acts to minimise the surface free energy i.e. causes the droplet to resist an increase in the surface area. This in turn causes an increase in the internal pressure of the droplet and therefore an increase in $\Delta P$. For a spherical droplet, $\Delta P$ can be expressed as follows:

$$\Delta P = \frac{2\gamma}{r}$$  \hspace{1cm} \text{Equation 49}$$

Therefore the smaller the particle, the greater the internal pressure (and consequently $\Delta P$) which means it is in fact more energetically favourable for particles to coalesce, since droplets are more stable as $r$ tends to infinity. Therefore for the breakup of nano-sized grains to occur, large amounts of energy are required to overcome the high $\Delta P$.

Surface tension maintains the grains spherical shape as long as it exceeds the Coulombic force generated by unshielded charges within the droplet. Below the Rayleigh radius, $r_{\text{Rayleigh}}$, the Coulombic force becomes greater than the surface tension, $\sigma$, and can result in the ejection of positive charges or stimulate the fission of the droplet [151, 154]. This assumes no aerodynamic forces, which is reasonable for droplets < 1mm.

$$r_{\text{Rayleigh}} = \left( \frac{q^2}{64\pi^2\varepsilon_0\sigma} \right)^{\frac{1}{3}}$$  \hspace{1cm} \text{Equation 50}$$

where $q$ is the net charge in the liquid droplet. The Rayleigh equation can also be rearranged to consider the maximum charge capable of being stored in a droplet, $q_{\text{Rayleigh}}$, of a given radius:

$$q_{\text{Rayleigh}} = 8\pi(\varepsilon_0\sigma r^3)^{\frac{1}{2}}$$  \hspace{1cm} \text{Equation 51}$$

The surface tension, $\sigma$, of bulk Au is 1.21 N m$^{-1}$ [150], however, the surface tension of Au nanoparticles has been shown to be substantially higher, as 9.3 N m$^{-1}$ [162]. The $q_{\text{Rayleigh}}$ was determined for a range of grain radii as shown in Figure 68a, which was then used to deduce the net number of unshielded positive charges that will result in Rayleigh Charge instabilities for a range of grain radii (1 charge = 1.602 x 10$^{-19}$ C).
Figure 68: (a) Maximum possible charge (femto Coulombs) stored in a stable Au droplet, \( q_{\text{Rayleigh}} \), for a range of Au grain radii. (b) Maximum number of unshielded positive charges stored in a stable Au grain.

This data can then be used in combination with the electron and ion emission data to predict whether there is sufficient positive charges residing in the grains to result in Rayleigh charge instabilities.

6.6.2 Rayleigh Charge Instability in Grains

This section explores whether the emission of a greater number of electrons than positive ions could result in Rayleigh charge instabilities in the ablated Au grains that could ultimately culminate in their Coulombic fission into smaller nanoparticles. The hypothesis is that following UV or Green thermoelastic ablation of the thin film into grains, the emission of MPPE electrons and fewer positive ions leaves a net positive charge residing in the grains. If the positive charge within each grain is greater than the threshold charge that can be stored by a stable droplet (Rayleigh charge), then the grain can break up.

In order to establish the net charge within each grain, the total number of charges emitted by the film was required. The detection of electrons and ions using a Langmuir probe setup only provides data for the charges travelling normal from the target surface for the area of the Langmuir probe. Therefore to ascertain the total number of charges, the number of charges must be estimated for the hemisphere over the film surface. Anisimov developed a hydrodynamic model for adiabatic expansion of neutral species following laser ablation [80]. This model has since been successfully applied to charged species and to
nanoparticles [80, 82, 163, 164]. The flux of material, $F(0)$ along a given angle, $\theta$, can be described by the following equation.

$$F(\theta) = F(0) \left[ \frac{(1 + \tan^2 \theta)^{3/2}}{(1 + \kappa^2 \tan^2 \theta)^{3/2}} \right]$$

Equation 52

where $F(0)$ represents the flux detected by the Langmuir probe, orientated normal to the Au film surface and $\kappa$ describes the forward directionality of the expanding plasma. This equation has been discussed in more detail in Appendix A. Equation 52 must be integrated over all angles of the plume hemisphere, i.e. from zero to $2\pi$, to determine the total number of charges emitted, $N_{\text{total}}$.

$$N_{\text{total}} = \frac{2\pi d F(0)}{\kappa^2}$$

Equation 53

where $d$ refers to the distance between the Au film and the Langmuir probe. Values of $\kappa$ are dependent on a number of factors including laser pulse duration and spot size, as well as material properties. Values for $\kappa$ have been determined for a number of femtosecond studies and typically range between 2-5 [161]. It was recently found for femtosecond laser ablation of Ag, that the value of $\kappa$ for the plasma part of the plume was significantly lower than for the plume overall (4.0 compared to 2.4, respectively) [163]. A study using the Langmuir probe setup used in this thesis was used to determine the $\kappa$ value for thin metal films and found that the values fell within a range of 6 – 10 [165]. Therefore a $\kappa$ value of 8 was selected for the following calculations.

Since the Anisimov model describes the angular dependency of the emission of species travelling directly from the target to the probe, it is therefore only applicable to the MPPE electrons and the ions, and not to the thermionically emitted electrons. The electrons emitted via thermionic emission were detected at relatively long timescales following the thermoelastic breakup of the film into grains. Therefore the thermionic emission of electrons occurs primarily from these ablated grains and nanoparticles. Therefore further work is required to develop a model to describe the angular dependence of thermionic emission of electrons from grains. Therefore the total number of electrons emitted from the
Au film during laser ablation was only determined for MPPE electrons and the ions using the Anisimov model.

To ascertain the net charge in each grain, the total number of positive ions emitted was subtracted from the total number of MPPE electrons emitted and the net charge was divided by the number of grains within the ablated area. This calculation is based on the assumption that the emission of a single electron from the Au film grains results in a single unshielded positive ion in the grain.

The total number of MPPE electrons and ions ejected from the Au film was determined at UV, Green and IR wavelengths at the absorbed fluence of 0.3 J cm\(^{-2}\) (\(\phi_{\text{NP}}\)). These total numbers of emitted charges were generated from an ablated area of approximately 6 \(\times\) 10\(^{-9}\) m\(^2\) in a 20 nm thick film. This ablated area comprised of a number of grains with an average grain area of 7 \(\times\) 10\(^{-16}\) m\(^2\) (\(d_G\) 29 nm). Therefore this ablated area would comprise of approximately 8.5 \(\times\) 10\(^6\) grains. The net charge density per grain, \(q_{\text{Grain}}\), was determined by subtracting the total positive charge emitted from the total negative charge emitted and this net charge was divided by the number of grains.

The net charge density per grain, \(q_{\text{Grain}}\), was determined at the three laser wavelengths and compared to the Rayleigh charge stability for a grain of \(d_G = 29\) nm. The values for \(q_{\text{Grain}}\) could then be compared to \(q_{\text{Rayleigh}}\), in order to ascertain the stability of the grains, as shown in Figure 69. To clarify the image, the grey area represents the number of charges that can be stored in a stable grain for a given radius. Above this grey area represents the number of charges that would result in Rayleigh Charge instabilities in a grain of a given radius.

Figure 69 shows that following both UV and Green ablation, \(q_{\text{Grain}} > q_{\text{Rayleigh}}\) and therefore the grain can be deemed unstable due Rayleigh Charge instability. Conversely, following IR ablation \(q_{\text{Grain}} < q_{\text{Rayleigh}}\) hence the grains are deemed stable. Charge instability can be partially resolved with the emission of further positive ions, but no further ionic emission was detected with the probe. In this case, the charge build is substantial and therefore following UV and Green ablation, the Rayleigh charge instability can drive the Coulomb fission of the grains into smaller nanoparticles [153, 154, 166].
Figure 69: Graph comparing the number of positive charges per grain, $q_{\text{Grain}}$, following laser ablation at UV, Green and IR wavelengths. $q_{\text{Grain}}$ is then compared to $q_{\text{Rayleigh}}$, which is represented by the grey area. The grey area denotes a stable grain, outside of which represents an unstable grain. Note: only MPPE electrons and ions considered.

Figure 69 describes the net charge per grain when the total number of MPPE electrons and ions are accounted for. The thermoelastic ablation occurs on ultra-short time-scales, however, the time-scale of the grain break-up is unclear. If the breakup occurs shortly after thermoelastic ablation, the contribution of the MPPE electrons could be central to the break up mechanism.

Thermionic emission of electrons occurred on substantially longer time-scales (microseconds) but contributed five times more electrons than MPPE mechanism. The break up of grains into smaller nanoparticles must occur following thermoelastic ablation, but before the nanoparticles re-deposit onto the substrate surface. Figure 70 illustrates the charge build up in the grains when the MPPE and thermionic electrons and ions are accounted for.

Figure 70 compounds the evidence for a wavelength dependence of electron and ion emission. The inclusion of the thermionic electrons exacerbates the charge build up in the grains at UV and Green wavelength. Conversely, at IR wavelength, $q_{\text{Grain}} < q_{\text{Rayleigh}}$. It should be noted that the total number of thermionic emitted electrons were also calculated using a $\kappa$ value of 8.
Figure 70: Graph comparing the number of positive charges per grain, $q_{\text{Grain}}$, following laser ablation at UV, Green and IR wavelengths. $q_{\text{Grain}}$ is then compared to $q_{\text{Rayleigh}}$, which is represented by the grey area. The grey area denotes a stable grain, outside of which represents an unstable grain. Note: only MPPE electrons and ions considered. Note: total number of electrons and ions are considered.

Figure 69 and Figure 70 illustrate the likely contribution of Rayleigh charge instability to the Coulombic fission of the grains into smaller nanoparticles at UV and Green wavelengths. By volume, the Grain-Nanoparticle relationship showed that seven average sized nanoparticles formed from an average sized grain. By diameter, the Grain-Nanoparticle relationship showed that 2-3 nanoparticles were produced from each grain with an average diameter. Using the data in Figure 69, the Coulombic fission of grains into 2-3 smaller nanoparticles would result in smaller unstable nanoparticles that were above the Rayleigh Charge stability limit for the resulting nanoparticle radii.

The mechanism of Coulombic fission has been successfully imaged using shadowgraphy. Firstly, a tail forms from the charged droplet, from which a droplet or a stream of droplets can form that are smaller in size than the parent droplet [153]. It is noteworthy that these daughter droplets are typically equal in size to one another. As the droplets form, the mass and charge must be conserved. Some studies have reported small losses in mass (2%) and charge losses (20%) [167]. The charge loss is associated with the small quantity of mass that breaks away from the daughter droplets. Therefore, during Coulombic fission of the grains into smaller nanoparticles, the charge losses may be sufficient to result in stable nanoparticles as shown by Figure 71. These values were calculated for MPPE electrons and ions only.
The interpretation of the charge emission data indicated that the grains exceeded the Rayleigh Charge stability threshold following UV and Green laser ablation (i.e. $q_{\text{Grain}} > q_{\text{Rayleigh}}$). Following IR laser ablation, $q_{\text{Grain}} < q_{\text{Rayleigh}}$ and were therefore deemed stable. This data supported the hypothesis that following thermoelastic breakup of the Au film into the grains following UV or Green ablation, the grains endure Rayleigh charge instabilities which may cause the Coulombic fission into the smaller nanoparticles measured by SEM in Chapter 5.

The literature informed that the Coulombic fission of droplets can result in up to 20% loss in charges, which are confined within a small quantity of mass (2%). Accounting for these values resulted in the Coulombic fission of a grain into two stable nanoparticles with 7 nm radii ($d_{\text{NP}} = 14$ nm). The $d_{\text{NP}}$ that was measured from this Au film following UV and Green laser ablation were 13.7 and 13.0 nm, respectively. It is also important to consider the assumptions made when carrying out these calculations.

**Assumptions**

1. The interaction of impinging positive charges with a negatively biased probe will differ from the interaction of impinging negative charges with a positively biased probe. Interpretation of the current-time waveforms depends on the assumption that the impingement of a charge on the probe efficiently produces a current. However, the ionic radius of Au is relatively large (0.85 Å) along with
the substantially greater mass compared to an electron. This is an important consideration and warrants further investigation into the efficiency of current generation at a Langmuir probe by different charged species.

2. The expansion of the plasma has been described by the model developed by Anisimov to include a directionality factor, $\kappa$. This factor assumes the expansion of the plasma from the target material surface into a vacuum. However, thermionic emission was detected on long time scales following thermoelastic ablation of the film into the grains. Therefore the detection of thermionic emission of electrons will likely result from electron emission from ejected grains and nanoparticles. Therefore a model needs to be devised to accurately predict the angular dependency of the emitted charges by thermionic emission.

3. The calculations assume that following the subtraction of detected positive charges from the detected negative charges, the net remaining positive charge resides solely within the Au grains. This assumption discounts methods of charge neutralisation, such as collisions between ejected electrons and ions with each other.

4. The early detection of a positive charge has previously been attributed to the ionisation of surface contaminants on the target material during femtosecond laser ablation [168, 169]. The Au film surface will have a layer of deposited contaminants from the air, including H, O and C atoms. Therefore the signal detected at the Langmuir probe will include a contribution from such contaminants. Common practice with bulk materials would be to apply several laser pulses (below the ablation threshold) to the surface to remove the layer of contaminants prior to carrying out the required experiments. However, this was not possible with thin films, since the ablation threshold of the material is so low.

5. The Grain-Nanoparticle relationship was established in ambient air conditions, whereas the detection of the plasma was carried out under vacuum conditions. The expansion dynamics of a plasma are more complex in ambient conditions, since they are affected by the properties of the background atoms [170]. The collisions of the expanding plasma with the ambient gas will result in lower charge build up in the grains.
6.6.3 Plasma Emission Summary

The results in this chapter have highlighted the significant wavelength dependence of electron and ionic emission following ablation using UV or Green wavelengths compared to IR wavelength. Both MPPE and thermionic emission following UV and Green ablation resulted in a substantially higher number of electrons than following IR ablation. This trend was also observed for ionic emission.

The current-time waveforms produced for electron emission showed two peaks, the first of which was attributed to MPPE and the second of which was attributed to thermionic emission. The MPPE emission mechanism was verified by plotting a logarithmic plot of the peak intensity against the electronic current, where the gradients of the linear trendlines matched the expected number of photons required for the MPPE process at each wavelength. For UV, Green and IR, the number of photons absorbed for MPPE, \( n \), were 2, 2 and 4, respectively. The number of MPPE electrons detected increased from IR to Green to UV, which reflected their respective multiphoton cross-sections. A plot of the absorbed fluence against the number of MPPE electrons showed a crossover whereby the number of electrons detected at the Green wavelength increased beyond the number of electrons detected at the UV wavelength. The reason for this was based on the number of photons absorbed to equate to the same absorbed fluence at each wavelength. A plot of the number of absorbed photons against the MPPE electron current showed an identical emission rate at UV and Green wavelengths compared to at IR.

Thermionic emission of electrons occurred over longer periods and therefore was more dependent on the electronic temperatures and distributions. No thermionic emission peak was observed following an IR pulse, but the peak was present following both UV or Green pulses. This was attributable to the photon energy relative to the ITT of Au. At UV and Green wavelengths, the photon energy exceeds the ITT and leads to d-band excitation of electrons to the Fermi level and higher \( T_e \). The Richardson-Dushman equation for the rate of thermionic emission indicates a partial \( T_e^2 \) dependency and consequently results in a far
higher thermionic emission rate at UV or Green wavelengths compared to at the IR wavelength. The number of electrons emitted by thermionic emission was five times greater than the number emitted by MPPE.

Finally, the detection of ions produced a substantially lower current compared to the detection of electrons by several orders of magnitude. This may be due to the difference in interaction between the respective charged species and the probe. It may also be due to there being substantially fewer positive charges emitted than electrons. An interesting observation was the temporal coupling of the MPPE electrons to the ions. This resulted in relatively low measured kinetic energies of electrons and relatively high kinetic energies of the ions compared to other studies. It has however, been shown that the fast emission of ions can be indicative of Coulombic explosion [62]. The number of ions emitted was found to be substantially higher at UV or Green wavelengths, compared to at IR. The reason for the higher ionic emission was dependent on the number of electrons emitted at the relative wavelengths. With a greater number of electrons ejected, the material is left with an increase in the number of unshielded positive charges. To neutralise this charge, positive ions are emitted and therefore a greater fluence will result in a greater number of ejected ions. This is the same reason for the increase in the emission of all charged species with increasing absorbed fluence.

The measured charges were then used to determine the possible contribution of Rayleigh charge instability to the fission of the grains into smaller nanoparticles. The data evidenced that following UV and Green wavelengths, $q_{\text{Grain}} > q_{\text{Rayleigh}}$ and following IR ablation, $q_{\text{Grain}} > q_{\text{Rayleigh}}$. Therefore due to the substantially greater number of electrons emitted compared to ions, the grains produced at UV and Green wavelengths underwent Rayleigh Charge instabilities that could induce Coulombic fission of grains into nanoparticles. Studies have shown that during Coulombic fission, up to 20% of charge may be confined to 2% of the mass as the parent droplet breaks up into uniform daughter droplets. By accounting for such a loss, it was found that the grain could break up into two stable nanoparticles ($d_{\text{NP}} = 14$ nm). This matched the $d_{\text{NP}}$ values measured in Chapter 5, at UV and Green wavelengths, which were 13.7 nm and 13.0 nm, respectively.
6.7 Real-Time Visualisation of Material Ejection

There are many indirect methods of probing the laser ablation process, some of which have been shown in this thesis. However, schlieren imaging offers the potential for real-time visualisation of the ablation mechanism and debris evolution. The intention of this section was to develop a schlieren imaging setup that was capable of imaging the spatial and temporal evolution of the nanoparticle plume. The data collected throughout this thesis has indicated differing ablation mechanisms occurring at UV and Green wavelengths compared to at the IR wavelength. The possibility of imaging the ablation process at different laser wavelengths would provide further detail of the ablation mechanisms at play.

6.7.1 Schlieren Imaging

Initially, a shadowgraphy setup was developed, which was relatively simple to assemble and could be used to visualise the evolution of the shockwaves generated during laser ablation. However, shadowgraphy offers a shadow of an optical image, whereas schlieren imaging offers a real, detailed, optical image of the area of interest. Schlieren imaging takes advantage of the variations in refractive index caused by a disturbance or object, which acts to refract parallel light from their original path. These deflected rays result in a shifted image called a schliere.

The theory of schlieren imaging was discussed in Section 2.6.4 and the equipment setup was presented in 3.7. Visualisation of the ablation process is complex due to the small refractive index variations in gases compared to in liquids or solids [122]. Additionally, the plumes are small and thus result in short interaction lengths and small deflections [108]. This is further complicated by the requirement of this study to image ablation at relatively low fluences of thin films. For these reasons, the optical components of the schlieren setup must all be optimised to achieve the greatest resolution and sensitivity.
6.7.2 Setup Development

The schlieren imaging setup used in this study is shown in Figure 72. A set of spatial filters are used at the two focal points of the system. A slit is positioned at the focal point of the lenses L₁ and L₂. A knife edge is positioned at the focal point of the lenses L₃ and L₄. Light from the diode laser passes through the slit and is collimated by L₂ and passes through the area above the Au film. Any disturbance of this light by a schlieren object (S.O.) would refract the light from the collimated pathway. The light is then focused by L₃ onto the knife edge before the schlieren image of the S.O. is focused on the iCCD camera by L₄. The components of the setup will be discussed in detail later in this section.

The sensitivity of the schlieren system, S, is the variation in contrast, C, with respect to the refraction angle, θ, caused by the schlieren object (S.O.) as per Equation 54. The contrast, C, describes the ratio of the amount of light refracted by the schlieren object, ΔE, relative to general background level, E.

\[
S = \frac{dC}{d\theta} = \frac{f_3}{a} \quad \text{Equation 54}
\]

\[
C = \frac{\Delta E}{E} = \frac{f_3 \theta}{a} \quad \text{Equation 55}
\]

where \( f_3 \) refers to the focal length of lens, L₃, and \( \theta \) refers to the angle of refraction induced by the presence of the S.O. (Refer to setup shown in Figure 72.)
It is important to note that the contrast is independent of the actual slit dimensions, but is inversely proportional to the unobscured height of the image of the slit at the knife edge, $a$, as illustrated by Figure 73 (image from Settles [108]).

![Diagram showing the schlieren system](image)

**Figure 73**: Image from [108] showing the undisturbed source image focused on the knife edge and the weak source image that is displaced due to the presence of the schlieren object. The sensitivity of the schlieren system is inversely proportional to the height of the exposed source image, $a$.

An additional sensitivity factor is the minimum discernable contrast ($\Delta E/E$) that is visible in a schlieren image. By increasing the background level of illumination, the minimum discernable contrast is decreased and can reach as low as 2% [108]. The image illuminance $E$, is linearly proportional to the amount of knife-edge cutoff (assuming that the detector also holds a linear relationship with respect to illuminance), but the knife edge position does not change $\Delta E$, thus increasing the contrast.

When the schlieren setup was first assembled, the achievable contrast was insufficient to image the laser ablation of thin Au films. This prompted the review of each component to optimise the sensitivity of the schlieren setup.
**Illuminance**

The schlieren image illuminance, in the absence of the knife edge, $E_0$, is proportional to the light source luminance, $B$, and the width, $w$, and height, $h$ of the source slit. $E_0$ is inversely proportional to the focal length, $f_2$, and the magnification of the image relative to the measured test area, $m$.

$$E_0 = \frac{B \cdot w \cdot h}{m^2 \cdot f_2^2}$$

Equation 56

Therefore if the light source beam across the schlieren area is small, then $m^2$ is minimised and $E_0$ is maximised. However, the trade-off with minimising the beam width is that the divergence of the beam is greater. Determining the slit dimensions is also a trade-off; it is imperative that the slit dimensions are smaller than the initial source of light at the focus of $L_1$, since the defined shape is matched to the sharp edge of the knife to achieve optimal schlieren imaging. However, smaller slit dimensions result in the blocking of light which consequently diminishes the background illuminance.

To maximise the light that passes through the slit, the condenser ($L_1$) and slit position were adjusted until the smallest spot size that still covered the entire slit was achieved. If the diameter of the focused spot, $d_0$, is defined as the diameter that contains 86% of the focused energy, the focus spot size, $d_0$, is determined by:

$$d_0 = \frac{2 \cdot f_1 \cdot \lambda}{D}$$

Equation 57

where, $f_1$ is the focal length of $L_1$, $D$ is the entrance beam diameter, and $\lambda$ is the wavelength. Therefore a small spot size was achieved by using a condenser lens ($L_1$) with a 50 mm focal length and the large beam diameter from the diverging diode laser.

The illuminance of the schliere at the iCCD was further enhanced by the MCP gain which maximised the signal: noise ratio. The maximum gain value (255) was required in order to image the ablation plume.
Lenses

Firstly a lens with a low f/number was selected as the condenser (L_1, f/number 1.14), since it gathers the maximum amount of the diode laser light. The f/number refers to the focal ratio of the focal length of the lens, f, to the diameter of the lens, d. The lens, L_2, was required to collimate the beam across the schlieren area. A longer focal length resulted in a larger beam with lower divergence, but this reduced the depth of field of the image and also the background intensity for the image. Therefore a compromise was sought to achieve light collimation with the minimum f/number.

The selection of L_3 is imperative in terms of the sensitivity of the setup. A longer focal length increases the sensitivity of the system as per Equation 54. However, the magnification and field of view of the schlieren area is dependent on the distance of the schlieren object to L_3, relative to f_3. The longer the distance, the smaller the magnification and the larger the field of view. This means that if the f_3 is long, the sensitivity will be improved as per Equation 54, but the collimated area can get very long and consequently result in divergence. Additionally, when a lens with a longer focal length (250 mm) was used as L_3, the greater contrast was diminished by the lower luminence.

Imaging small schlieren objects can result in imaging issues due to diffraction smearing. The image becomes increasingly blurred with a longer wavelength and a decreasing object size, which was a problem encountered during imaging of the ablation zone.

Spatial Filters

It was imperative for optimum imaging to place the slit and the knife-edge in the focal position of the respective lenses. When the slit is in the optimum position, the light emerging from the slit is spherical and homogeneous and the image of the slit is in focus at the knife-edge position. When the knife-edge is in the optimum position, the image darkens uniformly as the knife-edge is raised. If the knife-edge is placed out of focus, the knife-edge is visible on the CCD image. The uniform darkening was monitored using a cross-sectional plot of the image.
intensity. The width of the slit defines the width of the measuring range, but does not effect the sensitivity or the background illuminance, which is determined by the knife edge position [108].

**Camera**

The camera is a vital part of the schlieren setup and must have the appropriate temporal and spatial resolution for the required imaging. The Andor iCCD specifications were discussed earlier in Section 3.7.1 and allows control (0.5 ps) of delays and gate widths. The MCP gain can also help to maximise the signal to noise of the schliere despite relatively low luminance. The optimum schliere was achieved with the highest MCP gain of 255.

The spatial resolution of the system is measured in lines / mm and the lenses and camera all must be selected accordingly depending on the required imaging area. The resolution is dominated by the optical quality of the lenses and camera within the optical system and thus high quality Nikon lenses were selected. The Andor iCCD camera has 1330 x 512 pixels, and when imaging an area of approximately 1 mm$^2$, this results in approximately 1330 lines/mm in the vertical direction.

**Schliere Focus**

If the distance from $L_3$ to the schlieren object, S.O. is greater than the focal length of $L_3$, then a real schlieren image appears just after the knife-edge. The camera and $L_4$ position must then be adjusted so that the schlieren image is at the focus of this lens. This can be achieved by placing an object, in this case a bolt, at the position of the incident femtosecond laser pulse. When the knife-edge is raised, a diffraction halo occurs around the opaque object, which can be brought into sharp focus by adjusting the lens/camera position. An example of the observed diffraction halo is shown in Figure 74a. Once in focus, the bolt could be replaced with the target material and laser ablation could be carried out. Schlieren imaging was first achieved of the laser ablation at high laser fluences of a silicon wafer and of black card. Using high fluences and a bulk material facilitated simpler imaging owing to the generation of large quantities of debris.
Example schlieren images taken with the described schlieren setup are presented in Figure 74b and c of laser ablation of silicon and of a black card, respectively.

![Example schlieren images](image)

**Figure 74**: Example schlieren of (a) the focused diffraction halo resulting from an opaque object (bolt) and of (b) the expansion of the shockwave and debris 4 microseconds after IR laser ablation of a silicon wafer and (c) the expansion of debris 20 microseconds after IR laser ablation of black card.

### 6.7.3 Imaging of Thin Film Ablation

The imaging of laser ablation of the 20 nm thick Au films at the low fluences used in this study were unfortunately beyond the reach of the schlieren setup developed. Therefore to examine the wavelength dependence of laser ablation of Au, a 90 nm thick Au film on Quartz was selected. However, relatively high fluences and long gate width (1 µs) were required to achieve imaging. Post-processing of the images was also carried out as described in Section 3.7 to enhance the contrast of the images.

The Gaussian spot size, \( \omega_0 \), was determined as 44 µm, 49µm and 42 µm, at UV, Green and IR laser wavelengths, respectively. The absorbance at UV, Green and IR wavelengths had been determined in Chapter 4 as 64%, 27% and 3%, respectively. Therefore the applied laser fluences were 1.26, 2.96 and 26.6 J cm\(^{-2}\), which equated to absorbed laser fluences of 0.8 J cm\(^{-2}\) at each laser wavelength. No damage to the substrate beneath was observed following ablation.

Images of the nanoparticle plume expansion following UV, Green and IR laser pulses are shown in Figure 75, Figure 76 and Figure 77 respectively. Please note
the differing time-scale used for the plume expansion at IR laser wavelength. All times were determined relative to the time of arrival of the femtosecond laser pulse, $t_0$, as determined using a photodiode. The height of each image is 1.65 mm. The four images for UV and Green ablation occur over 2 µs, whereas the four images for IR ablation occur over 8 µs following the arrival of the laser pulse.

It was notable that the imaging of nanoparticle plume expansion was significantly easier following the IR laser pulse compared to either Green or UV pulses. This was attributed to the differences in the expansion of the plumes. The dense plumes produced at IR (Figure 77) results in a steep gradient in the refractive index and therefore a greater achievable contrast for schlieren imaging. Following an IR laser pulse (Figure 77), the nanoparticle plume expanded relatively slowly and all of the material remained within the dense, largely spherical, plume for over six microseconds. This equated to a relatively slow expansion rate of 80-100 m/s.

However, following UV (Figure 75) and Green (Figure 76) pulses, the material expansion was spatially non-uniform and culminated in the break up of the plume. Following just 500 ns (second image), some of the plume broke away with an expansion rate of approximately 600 m/s. The dispersion of the material resulted in a weaker achievable contrast and therefore more post-processing of the images was required in order to visualise the plume dynamics.
Figure 75: Evolution of nanoparticle plume following UV laser ablation of 90 nm thick Au film on Quartz with 1 µs gate width and a gate delays of 0, 0.5, 1 and 1.5 µs following the arrival of the femtosecond laser pulse. The dimensions of the images are 1.25 x 1.65 mm.

Figure 76: Evolution of nanoparticle plume following Green laser ablation of 90 nm thick Au film on Quartz with 1 µs gate width and a gate delay of 0, 0.5, 1 and 1.5 µs following the laser pulse. The dimensions of the images are 1.25 mm x 1.65 mm.

Figure 77: Evolution of nanoparticle plume following IR laser ablation of 90 nm thick Au film on Quartz with 1 µs gate width and a gate delay of 0, 2, 4, 6 µs following laser pulse. The dimensions of the images are 1.25 mm x 1.65 mm.
To achieve schlieren imaging of the laser ablation of the thin Au films, relatively long gate widths were required (1 µs). It is clear for all wavelengths that there is a great deal of expansion dynamics has already occurred within the first microsecond. At UV, Green and IR wavelengths, the plume has already expanded at approximately 310 m/s, 330 m/s and 243 m/s within 1 µs of the laser pulse. Therefore the microsecond gate width has obscured the details of this initial material ejection and plume expansion.

To reduce the gate width, the sensitivity of the schlieren setup must be significantly improved. This improvement is particularly important if schlieren imaging of the material ejection following laser ablation at $\phi_{NP}$ of a 20 nm Au film at all three laser wavelengths is to be achieved. To achieve these goals, future developments to the setup are proposed in the following section.

Despite the limitations of achievable sensitivity using this setup, the development has delivered some key information regarding the wavelength dependence of laser ablation of thin Au films. This thesis has compiled data regarding the wavelength dependence of laser ablation for 20 nm thick Au films. However, it is evident from the schlieren images that this fundamental difference extends to thicker Au films also. It is evident that the expansion of the laser generated plume differs following IR ablation compared to either UV or Green ablation. Additionally, the schlieren images were collected following laser ablation at substantially higher fluences than the ranges used throughout this study, but the wavelength dependence is still evident. Although the details of the images do not deliver clarification of the laser ablation mechanisms discussed throughout this study, it does show that the wavelength dependence of laser ablation is fundamental to the Au material. In particular these images support the hypothesis that the absorption of laser energy and the subsequent ablation is dependent on the interaction of the photon energy with the electronic system of the material.
6.7.4 Future Developments

Schlieren imaging holds the exciting potential to gain a clear picture of the laser ablation process. Further development of the setup would potentially glean higher contrast and temporal resolution. Proposals for improvements to the setup would require further investment and potentially could include the following:

- Longer focal length lens (L₃) would improve the contrast of the images as per Equation 55. However, this must be coupled with a light source with greater luminescence than the Cavitar laser can currently provide. An additional factor would be extension of the collimated beam required and thus L₂ would potentially require a longer focal length to achieve this, which would result in a greater beam width size. All these factors would substantially lengthen the setup and therefore the logistics must be considered.

- The threshold for discernable contrast is lowered if there is high luminescence. This could potentially be achieved with an alternative light source. Given the relative small size of the schlieren area of interest, a laser light source would be deemed suitable in terms of the beam diameter, luminescence, and temporal control. However, the use of a knife-edge is too harsh with coherent light and results in imaging problems such as fringes and coherent noise artefacts. However, this may be overcome using alternative graded filters in place of the knife-edge. Alternatively a Fischer Nanolite plasma discharge lamp can be used to get millijoules of visible light with 18 ns pulses. The use of visible light also has the added advantage of producing colour schlieren images.

- Alternative source filter combinations could be considered particularly in the case of a laser light source, namely the Hoffmann modulation filter in combination with a slit. Hoffmann modulation contrast filters, which are commonly used in microscopy, have been shown to intensify the contrast produced by small deviations compared to a knife edge [122]. A
Hoffmann filter comprises of three areas that transmit different amounts of light; the knife-edge that transmits 0% of light, and the window that transmits 100% of light surrounds a narrow grey filter, which transmits 15% and provides sufficient background intensity for the image. This filter comprises of three sections; the first transmits 100% of the light, the next transmits 15% light and then the knife transmits 0% of the light. This middle part allows sufficient light through to provide background intensity and phase gradients.

- Post-processing of images can be used to increase the discernable contrast of schlieren images. Various post-processing techniques have been investigated in the fields of astronomy and medical imaging and should be explored to minimise artefacts and improve the contrast of schlieren imaging of laser ablation.
6.8 Conclusions

• Two distinct peaks were discerned from the current-time waveforms produced following UV or Green laser ablation of a 20 nm Au film, but only one peak was observed following IR laser ablation.

The first peak observed at all three laser wavelengths was attributed to electrons emitted by multi-photon photoemission. This was verified by the log-log plot of laser intensity against number of electrons, with the gradients of each linear trendline relating to the number of photons absorbed by each electron at each respective wavelength. The second peak observed was attributed to the thermionic emission of electrons. This was achieved at UV and Green wavelengths but not at IR wavelengths owing to the greater electron temperatures reached following d-band electron excitation.

• A plasma was generated following the laser ablation of the 20 nm Au film at all three laser wavelengths.

The detection of the first emission peak of electrons occurred simultaneously with the detection of the positive Au ions. This implies that a plasma has formed above the surface and that the emitted electrons are coupled to the heavier positive ions. However, the current generated by the electrons was an order of magnitude greater than the current generated by the ions. This may be due to the differing interactions between the charged species and the probe or it may be as a result of a greater number of electrons emitted than positive ions.

• The emission of electrons and ions from an Au film was dependent on the photon energy of the laser pulse absorbed.

Electrons and ions were emitted during laser ablation of the Au film at all wavelengths. However, a greater number of both electrons and ions were emitted following the absorption of laser pulses with UV, followed by Green and finally IR wavelengths. The increase in electron emissions
related to the increasing photon energies of IR, Green and UV photons, whereby a higher photon energy facilitates the electrons to overcome the work function of the material either by MPPE or thermionic emission. The result of electron emission is unshielded positive charges in the Au material, which can be partially reduced through the emission of positive ions.

- **Evidence was found for Rayleigh-Charge instabilities to contribute to the break up of the grains into smaller nanoparticles following thermoelastic laser ablation.**

  The Rayleigh radius describes the balance between the surface tension of the ejected grains relative to the increasing Coulomb repulsion of charges within a spherical droplet. The net positive charge was determined per grain based on the charges detected with the Langmuir probe following laser ablation at each wavelength with $\phi_\lambda = 0.3$ J cm$^{-2}$. It was found that $q_{\text{Grain}} > q_{\text{Rayleigh}}$ following UV or Green laser ablation. Therefore it was deduced that the Rayleigh charge instability could induce Coulombic fission of the grains into the smaller nanoparticles that were measured in Chapter 5. It was also found that following IR ablation $q_{\text{Grain}} < q_{\text{Rayleigh}}$ and the grains were therefore deemed stable. This, once again, highlighted the significant differences between laser ablation of Au at UV or Green wavelengths compared to IR wavelength.

- **A schlieren imaging setup was developed and successfully applied to achieve real-time visualisation of laser ablation of a 90 nm Au film and highlighted the fundamental differences in material ejection of laser ablation of Au at different laser wavelengths.**

  Schlieren images were taken of nanoparticle plume expansion following laser ablation of a 90 nm Au film at an absorbed fluence of 0.8 J cm$^{-2}$ at three laser wavelengths. Despite the thicker film and the higher fluences than used in the rest of this study, the images compounded the fact that the difference in ablation was due to the fundamental interaction of photons with the electronic system of Au. At IR wavelength, the plume was spherical and dense and expanded relatively slowly (80-100 m/s).
Whereas at UV or Green laser wavelengths, the plume was non-uniform and partially broke away and moved away from the target at a much higher velocity (600 m/s).

- **Schlieren imaging holds the potential for real-time visualisation of laser ablation of any material, if the sensitivity can be improved.**

  A list of setup developments was proposed in order to enhance the sensitivity and the temporal control with the current setup but retain the high resolution. If the proposed developments prove successful, the schlieren imaging setup would prove an invaluable tool for the visualisation of laser ablation of all materials and laser conditions.
Chapter 7
Conclusions and Future Work

The key conclusions derived from the results in this thesis were presented at the end of each results chapter. The purpose of this section is to present the key results in the context of the state-of-the-art in the literature and to identify their potential impact.

7.1 Experimental Design

The original objectives of this study were to explore the influence of grain microstructures and laser wavelength on laser ablation, but particularly nanoparticle generation. Novel experimental design was required to explore these factors and minimise the variables. For example, comparison of laser ablation at different wavelengths has previously been carried out in the literature [95, 97, 123] and the methodology typically employed overlooks the variation in material optical properties at different wavelengths and thereby obscured potentially fundamental differences. This study has attempted to overcome this issue by measuring the reflectance from Au films using an Integrating sphere and calculating the transmittance through the film, thereby deducing the portion of laser light absorbed by the material. In knowing the absorption by a material, it is then possible to deduce the laser fluence absorbed by each material. The use of absorbed laser fluence, rather than the applied laser fluence, should be commonplace in the literature, since it allows simple comparisons to be drawn between laser ablation of different materials under different laser conditions.
The importance of the grain microstructure in the laser ablation process and nanoparticle generation has never previously been reported in the literature. The study required the fabrication of Au films with a range of grain microstructures, which was achieved through two successful applications for funding through the National Access Programme (NAP) and EUMINAfab. Through the NAP access programme (Tyndall, UCC) it was possible to deposit Au films on a range of substrates. Through the EUMINAfab programme (Phillips, Eindhoven), a number of Au films were fabricated using different deposition temperatures and rates. A set of fabrication conditions were selected, based on AFM results, which provided a matrix of Au films with a range of grain sizes. AFM proved a crucial tool for imaging the film topography, from which a method was devised for measuring the dimensions of the grains.

The method of nanoparticle collection used in this study also differed from those standardly applied in the literature. Commonly a substrate is orientated above the target surface and the nanoparticles deposit in a manner mimicking pulsed laser deposition. Every collection method induces bias onto the size distribution and number of nanoparticles collection. The placement of a substrate in the path of the expanding nanoparticle plume can result in the particles with high velocity and in a molten phase impacting onto the substrate. This became particularly evident through calculations of the cooling time of molten, nano-sized, droplets of Au based on its emissivity, which showed that the droplet can remain in molten phase for several milliseconds. If the particles are in the molten phase, surface energy dynamics (i.e. contact angle) with the substrate will influence the perceived size of the nanoparticles. Equally, the high speed can result in the nanoparticles rebounding from the substrate. Therefore this study monitored the nanoparticles that re-deposited onto the exposed substrate surface following ablation. The purpose of this method was to allow sufficient time for the nanoparticles to re-solidify and re-deposit onto the surface. The results showed that the average distributions (standard deviation/mean) of the nanoparticles collected fell within the same range of between 0.5 and 1, as was found using the alternative collection method employed by Amoruso [46].

Since the Au nanoparticles were collected on a non-conducting substrate, imaging of the nanoparticles using SEM was complex due to charging effects.
Typically a coating of conducting film (e.g. Au) would be applied to the sample of interest, but clearly this was not possible for this case. Therefore access was gained to a Carl Zeiss SEM in CRANN, TCD, Dublin and the combination of very low accelerating voltages, an In-Lens detector, small aperture size and low working distance facilitated the imaging of the nanoparticles.

During this study, two laser setups were developed to probe different aspects of the laser ablation process. The first was a Langmuir probe vacuum setup to detect the plasma emission during laser ablation and the second was a schlieren imaging setup to image the evolution of the nanoparticle plume in real-time. Both of these setups required control over the temporal alignment (nanosecond time-scales) of the femtosecond laser pulse with other pieces of equipment such as the oscilloscope, other lasers or a camera. The setups also required the careful spatial alignment (micron-scale) of the femtosecond laser pulse with the detection equipment, such as the Langmuir probe or the camera.

The development of the Langmuir probe setup facilitated the detection of both electron and ion emissions during laser ablation. A temporal profile could be generated of the detected charged components, from which the number and the emission mechanisms could be deduced. The setup was used to compare the plasma emission from thin Au films at different laser wavelengths.

The development of the schlieren imaging setup proved a very insightful tool for examining the laser ablation process and particularly the evolution of nanoparticle debris through the air. Previously, schlieren imaging was only used to image the laser ablation using a large (500 µm) spot size and relatively high fluences [122, 171]. In this study, schlieren imaging was achieved of the nanoparticle plume expansion following laser ablation of thin Au films at a more commonly applied spot size of approximately 40 µm. This study has shown that schlieren imaging is an under-utilized tool for probing laser ablation. Limitations to the achievable sensitivity of this schlieren imaging setup were unfortunately reached, primarily due to the low quantity of debris produced from thin films, the small changes in refractive index and the low fluences applied. However, developments were proposed in Section 6.7.4, which may allow the real-time visualisation of laser ablation of thin Au films and on shorter time scales. This
would facilitate direct comparisons of laser ablation at different laser wavelengths and is a useful tool for exploring laser ablation and nanoparticle generation.

7.2 Material Ejection from Au Films

The commonly used applied ablation threshold fluence, $\phi_{th}$, of a material has been replaced in this study by the absorbed ablation threshold fluence, $\phi_A$. The application of this parameter helped to identify the dependence of the absorbed laser ablation threshold fluence, $\phi_A$, on the film thickness and adhesion strength but relative independence on the grain microstructure, laser wavelength and substrate.

The linear increase in $\phi_A$ with Au film thickness showed that the threshold energy for material removal was linearly related to the amount of material to be removed. All material within the ablated crater was removed with a single laser pulse, regardless of film thickness. To exceed $\phi_A$, a threshold energy (4.97 eV) was evaluated that must be absorbed by each Au atom in the film. This value equates to the work function of Au (4.8-5.0 eV) and therefore it was proposed that the onset of material ejection is reliant on the ejection of electrons from the material. The high number of electrons ejected from the Au films was measured using a Langmuir probe under vacuum conditions. Results showed that the electrons were ejected by two mechanisms; initially via multiphoton photoemission (MPPE) and later by thermionic emission. Results also contributed to the understanding of the nanoparticle formation at different laser wavelengths that will be discussed in the later section.

Following plasma emission, Au material is ejected into the ambient. The evolution of the ejected material depends heavily on energy with which it is ejected, and also impacts the material phase and velocity. In the fluence range applied in this study, it was deduced that the temperature of the ejected material did not exceed the vaporisation temperature. The latent heat of melting and vaporisation for Au is 2.86 and 9.25 kJ cm$^{-3}$ respectively. The energy density
required to be absorbed to stimulate material ablation was calculated as 4.46 kJ cm$^{-3}$, which is sufficient to induce melting but not vaporisation. Additionally, the temperature of the electrons that were thermionically emitted from the material was deduced using the Richardson-Dushman equation and were also found to fall within the melting and vaporisation temperature of the Au material. Since the energy from the electrons is coupled to the lattice, the lattice cannot exceed the vaporisation temperature either. This was further substantiated with the detection of the grain-nanoparticle relationship, which showed a relationship in the size between the grain microstructure of the film and the nanoparticle debris. The existence of this relationship eliminates the possibility of material vaporisation since the relationship would be lost. The significance of this relationship is discussed further in the following section.

### 7.3 Grain-Nanoparticle Relationship

A key result in this thesis was the relationship between the size of the grain microstructure of the Au films with the size of the nanoparticles produced during laser ablation with a UV or Green laser pulse. This result became even more significant with the discovery that the relationship does not exist at the IR wavelength. The experimental data collected in this study was coupled with computational work carried out by several groups [40, 48, 53, 140] and in particular a model based on the non-equilibrium dynamics during laser ablation of a 20 nm Au film by Lin and Zhigilei [48]. This model was used to explain the wavelength dependence of the grain-nanoparticle relationship. The grain-nanoparticle relationship was explained through the different mechanisms for absorption and ablation occurring at each laser wavelength.

Absorption of laser energy by the electronic system of Au (5d$^{10}$6s$^1$) is dependent on the photon energy supplied. Photons with $h\nu < 1.9$eV deliver insufficient energy to achieve d-band excitation and thereby only s-band electrons are excited in an intraband process. Photons with $h\nu > 1.9$eV exceed the interband transition threshold (ITT) for d-band excitation, resulting in relatively strong absorption. According to Fermi’s Golden rule, the higher density of states associated with
the d-band compared to the s-band results in a greater absorption strength and heat capacity when the ITT is exceeded. Therefore when the ITT is exceeded, a higher $T_e$ is reached, which results in a greater temperature gradient between the electrons and lattice and therefore a higher $G_{ep}$.

The energy of UV (3.62 eV) and Green (2.41 eV) photons exceed the ITT resulting in high $T_e$ and fast electron-phonon coupling. Fast coupling (~1 ps) induces thermoelastic stress, which culminated in the break up of the film into the grains, thus retaining a relationship between the grain size and the nanoparticle size. The build up of thermoelastic stress occurs on shorter time-scales than mechanical relaxation (~5 ps) and thereby results in the break up of the film into grains. Phase changes of the material typically occur on even longer time-scales (ns) and calculations in this study determined that the temperatures reached exceed the melting temperature of Au, but not the vaporisation temperature. The lowest surface energy configuration for a melted grain is a sphere and calculations based on Au emissivity showed that Au droplets can remain in the molten state for several milliseconds before cooling and re-solidifying.

The energy of IR photons is insufficient to achieve d-band absorption and hence a relatively low $T_e$ is reached and electron-phonon coupling occurs over a relatively long time-scale. The longer time-scales result in the melting of the film that eliminates the grain boundaries before the onset of ablation and nanoparticle formation. This thereby removes any possible relationship between the size of grains with the size of nanoparticles.

The grain-nanoparticle volume relationship indicated that seven average-sized nanoparticles were produced for every average-sized grain from a 20 nm thick Au film. This result showed that following thermoelastic ablation of the film into the grains, further breakup ensued before resulting in the final nanoparticles. The exact number of nanoparticles produced per grain is biased by the collection method employed, as discussed in Section 7.1. Several mechanisms were considered that may result in the break-up of the molten grains into smaller nanoparticles. Rayleigh charge instability stems from the emission of electronic charge from a droplet, thereby resulting in build up of unshielded positive
charges within the grain. The Rayleigh charge, $q_{\text{Rayleigh}}$, determines the maximum charge that can be stored in a spherical droplet with a given radius. To explore the potential contribution of Rayleigh charge instabilities to grain breakup, the electronic and ion emission was monitored at the three laser wavelengths. The number of electrons emitted at UV and Green wavelengths far exceeded the number emitted at IR wavelength, primarily due to the thermionic emission of electrons. The higher thermionic emission at UV and Green wavelengths was due to the higher electron temperatures reached. There were also a substantially greater number of electrons detected compared to ions, by several orders of magnitude. The calculations of the Rayleigh charge instability in the grains was determined from the net positive charge per grain in the ablated area of the film. The number of ions was subtracted from the number of electrons emitted and divided by the number of grains to give $q_{\text{Grain}}$. It was determined that at UV and Green laser wavelengths, $q_{\text{Grain}} > q_{\text{Rayleigh}}$ and therefore the grains were deemed unstable. However, at IR wavelength, $q_{\text{Grain}} < q_{\text{Rayleigh}}$ and therefore the grains were deemed unstable. Therefore this data indicated that at UV and Green wavelengths, Rayleigh charge instabilities may contribute to the break up of the grains following thermoelastic ablation into smaller nanoparticles.

This result is impactful in a number of laser fields, particularly with respect to laser-material interactions but also in the developing field of laser generation of nanoparticles. When considering the laser ablation of materials using ultra-short laser pulses, the electronic system should be considered. The current state of the art in industry when approaching ablation of a new material is to apply a range of laser parameters and identify a process window with the required results. However, this study demonstrates that studies of the laser-material interaction can be used to potentially predict the ablation mechanism and therefore the resultant material response. This is also important in the field of laser generation of nanoparticles, in which numerous studies are being carried out to optimise material, laser and ambient properties to improve the control of the nanoparticles produced during laser ablation. This study has identified how the grain microstructure and the laser wavelength can be manipulated to provide different nanoparticle sizes.
7.4 Wavelength Dependence of Thin Au Film Ablation

A number of methods have been employed in this thesis, each of which have provided compounding evidence that the mechanism for laser ablation of Au films at UV and Green wavelengths, differs from that at IR wavelength. A fair comparison between laser ablation at different wavelengths was dependent on controlling other variables. As stated previously, the most important variable to control was the laser fluence absorbed by the Au film at each laser wavelength.

The first insight into the wavelength dependent ablation mechanisms was gleaned from the existence of the grain-nanoparticle relationship discussed in the previous section. Following this, the electron emission during laser ablation of Au films was monitored using a Langmuir probe and also indicated clear differences at each wavelength. The current-time waveforms evidenced substantially higher electron emission at UV and Green wavelengths than at IR wavelength. The data also showed that MPPE occurred at all wavelengths, but thermionic emission occurred at UV and Green, owing to the higher electron temperatures reached, producing approximately five times more electrons than MPPE. There was also evidence of a higher number of positive ions emitted at UV and Green wavelengths compared to at IR. Finally, the threshold fluence for plasma emission was found to be substantially higher at the IR wavelength compared to UV or Green wavelengths.

Finally, schlieren imaging of the laser ablation of a 90 nm Au film was achieved. The absorbed fluences (0.8 J cm$^{-2}$) used were higher than those typically used in this study. However, the images still evidenced the same trend shown throughout this thesis, that the ablation mechanism occurring at UV and Green wavelengths are effectively the same, and differ entirely to that at IR wavelength. Following IR ablation, the nanoparticle plume was dense and expanded relatively slowly over 6 µs. However, at both UV and Green wavelengths, there was evidence that the plume breaks up as it expands. In testing a thicker film and higher fluences, this result shows that the wavelength dependence of laser ablation is fundamental to Au.
7.5 Future Work

Following on from this thesis, there is now opportunity to build on these results and probe the wavelength dependent ablation mechanisms and the generation of plasma and nanoparticles.

- **Compare the wavelength dependent grain-nanoparticle relationship for other noble metals.**
  
The importance of non-equilibrium electron dynamics has been well documented for the response of noble metals to a laser pulse. This experimental study has explored the impact of the photon energy of a laser pulse on the absorption by and ablation of Au films. Other noble metals, such as copper or silver, have interband transition thresholds of 2.15 eV and 4 eV respectively [172]. Using the three laser wavelengths in this study, d-band excitation would be possible for copper at UV (3.62 eV) and Green (2.41 eV) wavelengths, but not at IR wavelength (1.21 eV). However, d-band excitation in Ag would not be possible at any of the available wavelengths. The fabrication of Ag, Ni and Cu films with different grain microstructures would facilitate the same study on these two films to confirm the importance of d-band excitation on laser absorption, ablation mechanisms and nanoparticle generation. Work functions of Ag and Ni are very similar to Au – 4.26 and 5.15, respectively [173]. Additionally, it would be of interest to explore the wavelength dependence of nanoparticle generation for Au films with a continuous microstructure i.e. without grains.

- **Consider other spatial beam shapes to optimise and simplify the laser-material interaction**
  
The Gaussian laser beam shape used throughout this study causes variations in the laser-material interaction across the beam profile. A potential improvement to ablation efficiency and certainly a simplification of the laser-material interaction would be to apply a top-hat
beam profile. This would ensure a uniform temperature distribution across the film surface and consequently a more uniform ablation process.

- **Compare laser ablation and nanoparticle formation at different laser wavelengths, keeping the number of absorbed photons the same.**
  During this study, the same absorbed laser fluence was delivered to an Au film for three laser wavelengths. The resultant data highlighted the significance of the photon energy, but some results were potentially influenced by the increasing number of photons applied to the material at the different laser wavelengths. It would therefore be of interest to create a study into nanoparticle generation during laser ablation of Au, whereby the number of photons absorbed was the same, and only the photon energy differs.

- **Continue the investigation into the wavelength dependence of plasma emission from Au films using the Langmuir Probe setup**
  Evaluate the wavelength dependence of the angular emission of the plasma and electron temperature following laser ablation of Au films. Additionally, the impact of the laser fluence and film thickness could also be investigated in terms of the number density of electrons and ions emitted from differing volumes of ablated craters. It is also of interest whether the angular dependency of the electron emission differs to the positive ions. Additionally, it may be useful to select a pulse function curve fit as opposed to a Gaussian/Lorentzian mix to better fit the first peak observed for electron emission.

- **Develop schlieren imaging setup to achieve greater sensitivity and thus visualise the evolution of debris with shorter gate widths.**
  Although schlieren imaging of laser ablation with the setup discussed in this thesis, the limitations of imaging sensitivity was reached. However, a list of proposed developments to the schlieren setup were laid out in Section 6.7.4, which would potentially reward major advancements in
imaging sensitivity. The most impactful suggestions would be to apply laser illumination with a Hoffmann modulation filter.

- **Develop imaging setup to include spectroscopic information about expanding plasma, plume and nanoparticles.**
  An imaging setup was developed during this study that facilitates plasma emission imaging, shadowgraphy and schlieren imaging. There is now significant potential for the addition of a spectroscopic arm that can feed the light emission from the interaction zone into a spectrometer. The resultant spectra can deliver information about the chemical composition and temperature of the ablated components.
Appendices

A – Total Number of Charges

It is commonly understood that the plasma geometry can be described in three coordinates by the Anisimov hydrodynamic model for adiabatic expansion [80]. The model describes the plasma expansion starting as a thin elliptical disk above the target surface. This disk has dimensions of \( X_0, \ Y_0 \) and \( Z_0 \). The expansion of the plasma is considered isentropic and therefore there is no consideration of heat conduction within the plume. As time, \( t \rightarrow \infty \), the expansion of the plume in \( X(t) \) and \( Z(t) \) becomes inertial, and therefore the forward directionality of the plume can be described as \( \kappa(\infty) = X(\infty) / Z(\infty) \). For the detection of the plasma using a Langmuir probe, the flux of charges is typically measured normal to the target surface. The model can then be used to predict the flux across the hemispherical surface centered around the ablation crater [4].

The flux of material, \( F(\theta) \) along a given angle, \( \theta \), can be described by the following equation.

\[
F(\theta) = F(0) \left[ \frac{(1 + \tan^2 \theta)^{\frac{3}{2}}}{(1 + \kappa^2 \tan^2 \theta)^{\frac{3}{2}}} \right] \quad \text{Equation 58}
\]

where \( F(0) \) represents the flux detected by the Langmuir probe, orientated normal to the Au film surface and \( \kappa \) describes the forward directionality of the expanding plume.

Figure 78 provides a diagram of the calculation of the total number of charges emitted from the Au film, given the flux of charges to the Langmuir probe, orientated normal to the film surface at a distance, \( d \).
Figure 78: Image of the method for determining the total net charge emitted from the Au film during laser ablation based on the flux of charges detected by the Langmuir probe, orientated normal to the film surface at a distance d.

\[
F_{\text{total}} = d^2 \int_{\theta=0}^{2\pi} F(\theta) \sin \theta \, d\theta \int_{\phi=0}^{2\pi} d\phi 
\]

Equation 59

\[
F_{\text{total}} = 2\pi d^2 F(0) \int_{\theta=0}^{2\pi} \frac{(1 + \tan^2 \theta)^{3/2} \sin \theta}{(1 + k^2 \tan^2 \theta)^{3/2}} \, d\theta
\]

Equation 60

To determine the total flux of charges in the plume, \( F_{\text{total}} \), Equation 58 must be integrated over all angles of the plume hemisphere, i.e. from zero to \( 2\pi \), to give the total number of charges, \( N_{\text{total}} \).

\[
N_{\text{total}} = \frac{2\pi d F(0)}{k^2}
\]

Equation 61

where \( d \) refers to the distance between the Au film and the Langmuir probe.
**B - List of Abbreviations, Acronyms and Symbols**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>CPA</td>
<td>Chirped Pulse Amplification</td>
</tr>
<tr>
<td>DOF</td>
<td>Degrees of Freedom</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>Fs</td>
<td>Femtosecond</td>
</tr>
<tr>
<td>iCCD</td>
<td>Intensified Charge Coupled Device</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ITT</td>
<td>Inter-band Transition Threshold</td>
</tr>
<tr>
<td>MPPE</td>
<td>Multiphoton Photoemission</td>
</tr>
<tr>
<td>NED</td>
<td>Non-Equilibrium Dynamics</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>Ns</td>
<td>Nanosecond</td>
</tr>
<tr>
<td>Ps</td>
<td>Picosecond</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Squared</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>THG</td>
<td>Third Harmonic Generation</td>
</tr>
<tr>
<td>TTM</td>
<td>Two-Temperature Model</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab-Initio Simulation Package – Quantum mechanical Molecular dynamics model to describe electronic structures.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>A</td>
<td>Area of Langmuir Probe</td>
</tr>
<tr>
<td>A_s</td>
<td>Area of Integrating Sphere</td>
</tr>
<tr>
<td>B</td>
<td>Light source luminance</td>
</tr>
<tr>
<td>c</td>
<td>Speed of light</td>
</tr>
<tr>
<td>c_p</td>
<td>Specific heat at constant pressure</td>
</tr>
<tr>
<td>c_v</td>
<td>Electron volumetric heat capacity</td>
</tr>
<tr>
<td>d</td>
<td>Distance travelled by plasma species</td>
</tr>
<tr>
<td>d_g</td>
<td>Mean Diameter of Grains</td>
</tr>
<tr>
<td>d_n</td>
<td>Mean Diameter of Nanoparticles</td>
</tr>
<tr>
<td>d_s</td>
<td>Focused spot diameter</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>e</td>
<td>electron charge</td>
</tr>
<tr>
<td>E</td>
<td>Electric field vector</td>
</tr>
<tr>
<td>E</td>
<td>Energy</td>
</tr>
<tr>
<td>E_F</td>
<td>Fermi Energy</td>
</tr>
<tr>
<td>E_K</td>
<td>Kinetic Energy</td>
</tr>
<tr>
<td>E_p</td>
<td>Pulse Energy</td>
</tr>
<tr>
<td>f</td>
<td>Focal length</td>
</tr>
<tr>
<td>f</td>
<td>Port fraction (integrating sphere)</td>
</tr>
<tr>
<td>G_{ep}</td>
<td>Electron-Phonon coupling factor</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>I</td>
<td>Laser intensity</td>
</tr>
<tr>
<td>I_o</td>
<td>Peak Intensity</td>
</tr>
<tr>
<td>I_e</td>
<td>Current generated due to electrons</td>
</tr>
<tr>
<td>I_{es}</td>
<td>Electron saturation current</td>
</tr>
<tr>
<td>I_i</td>
<td>Current generated due to ions</td>
</tr>
<tr>
<td>I_{is}</td>
<td>Ion saturation current</td>
</tr>
<tr>
<td>I_p</td>
<td>Probe current</td>
</tr>
<tr>
<td>I_t</td>
<td>Total plasma current</td>
</tr>
<tr>
<td>J_e</td>
<td>Rate of thermionic emission of electrons</td>
</tr>
<tr>
<td>J_n</td>
<td>Rate of photoelectric photoemission</td>
</tr>
<tr>
<td>k</td>
<td>Imaginary part of the complex refractive index</td>
</tr>
<tr>
<td>k_B</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>K_e</td>
<td>Electron thermal conductivity</td>
</tr>
<tr>
<td>K_l</td>
<td>Lattice thermal conductivity</td>
</tr>
<tr>
<td>l_s</td>
<td>Optical absorption depth</td>
</tr>
<tr>
<td>m_e, m_i</td>
<td>Mass of electrons and ions</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>M²</td>
<td>Beam quality factor</td>
</tr>
<tr>
<td>n</td>
<td>Real part of the complex refractive index</td>
</tr>
<tr>
<td>nₑ</td>
<td>Electron density</td>
</tr>
<tr>
<td>Nₑ, Nᵢ</td>
<td>Number of electrons and ions</td>
</tr>
<tr>
<td>P</td>
<td>Average Power</td>
</tr>
<tr>
<td>q</td>
<td>Charge</td>
</tr>
<tr>
<td>Q</td>
<td>Repetition Rate</td>
</tr>
<tr>
<td>R</td>
<td>Reflectance</td>
</tr>
<tr>
<td>S</td>
<td>Sensitivity (schlieren imaging)</td>
</tr>
<tr>
<td>tᵢₒ</td>
<td>Time of incident pulse at target material</td>
</tr>
<tr>
<td>t</td>
<td>Time relative to tᵢₒ</td>
</tr>
<tr>
<td>T</td>
<td>Transmittance</td>
</tr>
<tr>
<td>Tₑ</td>
<td>Electron temperature</td>
</tr>
<tr>
<td>Tₑₛ</td>
<td>Surface electron temperature</td>
</tr>
<tr>
<td>Tₘ</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>v</td>
<td>Velocity</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>Vₑ</td>
<td>Mean columnar volume of Grains</td>
</tr>
<tr>
<td>Vₑₚ</td>
<td>Mean spherical volume of Nanoparticles</td>
</tr>
<tr>
<td>Wₑ</td>
<td>Work Function</td>
</tr>
<tr>
<td>Z</td>
<td>Charge state</td>
</tr>
<tr>
<td>α</td>
<td>Linear absorption coefficient</td>
</tr>
<tr>
<td>γ</td>
<td>Adiabatic Index (plasma)</td>
</tr>
<tr>
<td>Δ</td>
<td>Coulomb logarithm</td>
</tr>
<tr>
<td>ε</td>
<td>Emissivity</td>
</tr>
<tr>
<td>ε₀</td>
<td>Permitivity in free space</td>
</tr>
<tr>
<td>εᵣ</td>
<td>angle of deflected ray in y direction (schlieren)</td>
</tr>
<tr>
<td>θ</td>
<td>Flux of species at angle θ relative to surface normal</td>
</tr>
<tr>
<td>κ</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>λ₀</td>
<td>Debye Length</td>
</tr>
<tr>
<td>v</td>
<td>Velocity</td>
</tr>
<tr>
<td>ρ</td>
<td>Mass density</td>
</tr>
<tr>
<td>σ</td>
<td>Absorption cross-section</td>
</tr>
<tr>
<td>τₑ</td>
<td>Pulse Duration</td>
</tr>
<tr>
<td>ω₀</td>
<td>Gaussian Beam Radius</td>
</tr>
<tr>
<td>φ₀</td>
<td>Peak Fluence</td>
</tr>
<tr>
<td>φₑ</td>
<td>Absorbed Ablation Threshold Fluence</td>
</tr>
<tr>
<td>φₘₑ</td>
<td>Ablation Threshold Fluence</td>
</tr>
<tr>
<td>φₑₚ</td>
<td>Fluence for Nanoparticle generation</td>
</tr>
<tr>
<td>ωₑ</td>
<td>Electron Plasma Frequency</td>
</tr>
</tbody>
</table>
C - Publications and Other Outputs

Publications:


Patents:


Awards:

1. Poster Award: Nanoweek, County Kildare, January 2011,
2. Graduate Student Award – EMRS Spring Meeting, May 2011
Successful Applications for Funding:
1. IRCSET Embark funding for PhD studies
2. Application NAP347 - National Access Programme, Tyndall, Cork
   ‘Thin Gold Film Fabrication”
3. Application EUMINAfab 1061 – EUMINAfab, Phillips – MiPlaza –
   ‘Investigation into laser-material interactions, ablation mechanisms and
   nanoparticle generation during laser ablation of thin films’
4. OSA Student Travel Grant to Frontier in Optics and Lasers in Science in
   San Jose, California including the ‘Student Leadership Conference’.

Presentations
1. 2011 - Poster Presentation at Nanoweek, County Kildare, Ireland
2. 2011 - Oral Presentation at Lasers in Manufacturing, Munich, Germany
3. 2011 - Poster Presentation at EMRS conference, Nice, France
4. 2011 - Poster Presentation at Photonics Ireland, Malahide, Ireland
5. 2011 - Oral Presentation at the Frontier in Optics and Lasers in Science,
   (OSA 95th General Meeting), San Jose, USA
6. 2012 - Oral Presentation at EMRS Spring Meeting, Strasbourg, France
7. 2013 - Poster Presentation at EMRS Spring Meeting, Strasbourg, France

Structured PhD Modules

1. Nanotechnology
2. Statistical Methods
3. Teaching and Learning
4. Graduate Skills
5. Technical writing
6. NCLA Book and Journal Club
7. Campus Commercialisation Programme


135. Hastrup, N., Nanoparticle Generation During Laser Ablation of Thin Metal Films, in School of Physics 2010, National University of Ireland, Galway.
