Laser Filamentation Interaction With Materials For Spectroscopic Applications

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LASER FILAMENTATION INTERACTION WITH MATERIALS FOR SPECTROSCOPIC APPLICATIONS

by

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ABSTRACT

Laser filamentation is a non-diffracting propagation regime consisting of an intense core that is surrounded by an energy reservoir. For laser ablation based spectroscopy techniques such as Laser Induced Breakdown Spectroscopy (LIBS), laser filamentation enables the remote delivery of high power density laser radiation at long distances. This work shows a quasi-constant filament-induced mass ablation along a 35 m propagation distance. The mass ablated is sufficient for the application of laser filamentation as a sampling tool for plasma based spectroscopy techniques. Within the scope of this study, single-shot ablation was compared with multi-shot ablation. The dependence of ablated mass on the number of pulses was observed to have a quasi-linear dependence on the number of pulses, advantageous for applications such as spectroscopy. Sample metrology showed that both physical and optical material properties have significant effects on the filament-induced ablation behavior.

A relatively slow filament-induced plasma expansion was observed, as compared with a focused beam. This suggests that less energy was transferred to the plasma during filament-induced ablation. The effects of the filament core and the energy reservoir on the filament-induced ablation and plasma formation were investigated. Goniometric measurements of the filament-induced plasma, along with radiometric calculations, provided the number of emitted photons from a specific atomic transition and sample material.

This work advances the understanding of the effects of single filaments on the ablation of solid materials and the understanding of filament-induced plasma dynamics. It has lays the foundation for further quantitative studies of multiple filamentation. The implications of this
work extend beyond spectroscopy and include any application of filamentation that involves the interaction with a solid material
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LIST OF ACRONYMS

APG—Aberdeen Proving Ground

ARL—Army Research Laboratory

As—Arsenic

Au—Gold

CCD—Charge Coupled Device

DIAL—Differential Absorption LIDAR

EELS—Electron Energy Loss Spectroscopy

EDS—Energy Dispersive Spectroscopy

FIB—Focused Ion Beam

FROG—Frequency Resolved Optical Gate

FWHM—Full Width at Half Maximum

Ga—Gallium

GaAs—Gallium Arsenic

ICP—Inductively Coupled Plasma

ICCD—Intensified Charge Coupled Device

IR—Infrared
LA—Laser Ablation

LIBS—Laser Induced Breakdown Spectroscopy

LIPSS—Laser Induced Periodic Surface Structures

LIDAR—Light Detection and Ranging

LPL—Laser Plasma Laboratory

MPI—Multi-Photon Ionization

MS—Mass Spectrometry

PPB—Parts-Per-Billion

PPM—Parts-Per-Million

PTP—Peak-To-Peak

RMS—Root-Mean-Square

RSD—Relative Standard Deviation

SEM—Scanning Electron Microscope

SNR—Signal to Noise Ratio

SPM—Self-Phase Modulation

TEM—Transmission Electron Microscope
Ti—Titanium

TLI—Townes Laser Institute

UV—Ultraviolet

WIM—White light Interferometric Microscope
CHAPTER 1. INTRODUCTION

1.1 Motivation

This work was motivated by the potential application of laser filamentation for spectroscopy at stand-off distances and has advanced the understanding of how filaments interact with solid materials. Laser filamentation (CHAPTER 2) refers to a unique propagation regime within which the power density of the laser pulse remains constant along its path of propagation. Filamentation could extend the distance from which stand-off laser-ablation based spectroscopy techniques, such as Laser Induced Breakdown Spectroscopy (LIBS) (CHAPTER 3), could be employed.

Filamentation has been applied for LIDAR (Light Detection and Ranging) at a stand-off distance of ~ 4 km [1]. This demonstration of filamentation for stand-off sensing illustrated the potential as well as some of the challenges ahead:

1) For stand-off LIBS using filamentation, the emission from filament-induced plasmas is relatively weak (quantification presented in CHAPTER 7); therefore, the detection of the plasma emission at long distance is problematic—a signal-shot-noise limited detector with large, yet practical, detection aperture only leaves finite room for improvement.

2) The plasma temperature that is characteristic of filament-induced plasmas is lower than that commonly used for LIBS under focused conditions. This lower temperature plasma leads to a lower degree of ionization and a greater probability for the formation of radicals. In comparison to atomic and ionic emission, the spectral signatures from molecules are often non-representative of the sample composition.
3) Filament-induced ablation, as the sampling source for LIBS, has potential for fractionation and matrix effects—signal not representative of sample stoichiometry. Therefore, filament-induced plasmas used for stand-off LIBS are difficult to detect and from an analytical point of view potentially non-representative of the sample composition.

This research addresses the inherent challenges of using filamentation for spectroscopy through creating a better understanding of filament-material interaction science and lays the foundation from which filament-induced ablation and the plasma emission properties can be tailored. This research builds upon previous work completed within the Laser Plasma Laboratory (LPL) and answers the following questions:

1) How do the properties of filament-induced ablation compare with focused laser ablation?
2) How does the energy reservoir, that surrounds a single filament, influence the ablation of solids?
3) How much mass is ablated when a filament encounters a solid material?
4) How many photons are emitted from filament-induced plasmas—what is the radiance of the plasma?

The primary differences between the interaction of femtosecond (fs) laser filaments with solid materials as compared with focused fs laser radiation stems from the unique spatial-temporal properties of the filament. The stable filament has a near zero numerical aperture, and an irradiance ($10^{12}$-$10^{14}$ W/cm$^2$) that is sufficient to ablate nearly any material placed within its
path. The filament is supported by the energy contained within the surrounding energy reservoir, which contains only a fraction of the total beam energy.

1.2 Organization of document

This dissertation is divided into 8 chapters. The introductory material is included within the first three chapters. Following this introduction, CHAPTER 2 introduces Femtosecond Laser Filamentation and CHAPTER 3 introduces Laser Induced Breakdown Spectroscopy. Within these introductory chapters the necessary background information is presented from published literature. Within the next section, Experimental Facilities and Diagnostics (CHAPTER 4), an overview is given of the technical details of the experimental facilities and diagnostics. My original research work is presented in the next three chapters. The possible mechanisms for plasma emission enhancement in double-pulse LIBS are presented in CHAPTER 5. This double-pulse LIBS work illustrates the importance of laser-material interaction on the resulting plasma dynamics. Quantification of filament-induced material ablation is presented in CHAPTER 6 and the material sampled per shot is shown to be sufficient for laser ablation based spectroscopy applications. A correlation is presented between the filament fluence profile and the ablation crater. The expansion dynamics of filament-induced plasmas and filament-induced shockwaves are presented in CHAPTER 7 along with the quantification of plasma emission as a function of the detection angle. Finally, the Conclusion is given in CHAPTER 8.
CHAPTER 2. FEMTOSECOND FILAMENTATION

2.1 Introduction

Filamentation is a form of non-linear propagation that allows a beam to propagate without increasing in diameter. Chin [2] has proposed that a filament be defined as “the propagation zone where there is intensity clamping”. Filamentation requires a nonlinear medium and results from a dynamic balance between self-focusing and defocusing mechanisms such as diffraction and plasma defocusing (Figure 2-1).

![Figure 2-1. Cartoon illustration of filamentation dynamics. The dimensions shown are exaggerated to clearly illustrate the regimes of nonlinear propagation during the filamentation process: self-focusing leading to beam collapse, the oscillation between focusing and defocusing, stable filamentation and the discontinuation of filamentation.](image)

Filamentation begins with self-focusing within a nonlinear medium that results from an intensity dependent and spatially varying refractive index profile. To first order, the nonlinear refractive index profile experienced by an intense laser pulse is given by [3]:

\[ n = n_0 + n_2 I(r, t) \]  

(2-1)
where $n$ is the total refractive index, $n_0$ is the linear component of the refractive index and $n_2$ is the nonlinear component that is proportional to the spatially ($r$) and temporally ($t$) varying laser irradiance, $I(r,t)$. Because the non-linear refractive index, $n_2$, is only $5.6 \cdot 10^{-19}$ cm$^2$/W for air at atmospheric pressure and at 300 K [4], this non-linear effect is most apparent for high peak power ultrashort laser pulses. A pulse with a Gaussian shaped spatial intensity distribution will experience a Gaussian shaped refractive index profile—a refractive index profile that is highest on-axis. This refractive index distribution acts as a positive lens that causes the beam to self-focus. Self-focusing causes the beam to collapse when the pulse power exceeds the critical power threshold (Sec. 2.2.2) for the medium and the beam divergence from diffraction is overcome. Following beam self-focusing and collapse, the spatial intensity distribution becomes a ‘Townes’ spatial profile, as depicted by the cartoon illustration in Figure 2-2.

Figure 2-2. Self-focusing and filamentation of a femtosecond laser pulse

Self-focusing increases the irradiance until ionization of the medium occurs and an underdense plasma is formed. The plasma contributes negatively to the refractive index (Sec. 2.2.3) and, along with other mechanisms such as diffraction, will cancel the effects of self-focusing and lead to the formation of a filament (Figure 2-1). During the onset of filamentation, oscillation between focusing and defocusing mechanisms can modulate both the spatial extent of
the filament as well as the irradiance (Figure 2-1). Following this region of oscillation, the filament stabilizes. The stable filament is composed of an intense core with clamped irradiance that is surrounded by an energy reservoir (The spatial profile and relative fluence of the energy reservoir will be the topic of Section 4.5). For filamentation in air, the clamped core irradiance, on the order of $7 \cdot 10^{13} \text{ W/cm}^2$ [5], results in the ionization of oxygen and nitrogen and the formation of an underdense plasma (Figure 2-3). The filamentation region that is accompanied by plasma is followed by a less intense region where diffraction is partially compensated by self-focusing. This less intense region is often referred to as a ‘light channel’ and will be described further in Section 2.3.4.

Figure 2-3. A long-exposure photograph of the plasma emission that results during filamentation. Within a dark laboratory, the filament emission was visible to the dark adapted eye—detection primarily by the rods of the human eye and not the cones. The blue color was characteristic of molecular nitrogen emission bands in the 300 nm to 400 nm spectral region.
The mechanisms responsible for filamentation that were introduced above are described in more detail within Section 2.2 following a brief historical overview of self-focusing and filamentation (Sec. 2.1.1).

2.1.1 Historical development

The elimination of diffractive beam divergence through self-focusing was reported by Askar’yan in 1962 [6]. Laser induced damage in glass was reported by Michael Hercher at the Spring Meeting of the Optical Society of America in Washington, D.C. in 1964. Radiation from a Q-switched laser resulted in 2 cm long damage lines collinear with the beam [7]. Later in 1964, Chiao, Garmire and Townes published calculations for beam self-trapping based on a uniformly intense circular beam propagating in a Kerr medium [8]. The calculated distribution is commonly referred to as the Townes distribution (illustrated in Figure 2-2) and has been observed when self-focusing cancels the effects of diffraction. In the late 1960s, my advisor, Dr. Richardson, observed self-focusing in gases [9]. Self-focusing in N₂O and CO₂ gases was later reported in 1970 by Mack and Carman [10]. The clamped irradiance of a self-focused beam within transparent liquids was shown by Yablonovitch and Bloembergen in 1972 [11]. It was not until 1995 that Braun, et al [5] observed filamentation in air. They observed filamentation over a distance of 20 m using a laser system with 200 fs pulses, energies of 50 mJ per pulse and 10 nm wide spectrum centered at 775 nm. For initial pulse energies of 10 mJ, they observed filamentation starting 10 m from the compressor and propagating for an additional 20 meters. For energies above 20 mJ, multiple filaments were observed; however, when a clean spatial beam profile was used, only one filament was observed for up to 30 mJ. They measured energies of ~ 0.75 mJ per filament, a filament diameter (FWHM) of ~ 80 µm, critical power of ~ 10 GW
for the cancellation of diffraction effects and at 13.5 GW they observed beam collapse due to self-focusing. They assumed that the pulse duration during filamentation did not change with distance (This assumption is no longer consistent with the commonly accepted views of the filamentation community, as will be discussed in Section 2.3.3). This was inferred based on their observation of a constant spectrum during filamentation and because the positive group velocity dispersion associated with propagation roughly canceled the negative group velocity dispersion induced by the plasma. Based on the assumption of a constant pulse duration, they were able to calculate an irradiance of $7 \cdot 10^{13}$ W/cm² and their simulation results suggested that the irradiance was clamped as a result of the ionization threshold of air. At this intensity, the magnitude of the refractive index change was calculated to be $3.5 \cdot 10^{-5}$ and the density of the plasma necessary for the cancellation of self-focusing was calculated to be $4.5 \cdot 10^{16}$ cm⁻³[5].

In the years since the initial filamentation experiments by Braun, et. al [5], various applications have emerged: long distance propagation of ultrashort pulses [12-14], microwave guiding [15], LIDAR [16], Filament Induced Breakdown Spectroscopy (FIBS) [17], white light generation [18], THz generation [19], lightning protection [20] and the generation of high harmonics [21, 22]. Applications of filaments are the topic of section 2.4.

2.2 Filamentation physics

2.2.1 Kerr effect

The optical Kerr effect is the change in refractive index of a medium that is proportional to the laser irradiance and proportional to the square of the electric field. The non-linear Kerr index of refraction $n_2$ is proportional to the third order susceptibility as given by [23]:

\[ n_2 = \chi^{(3)} \]
\[ n_2 = \frac{3}{4} \frac{\chi^{(3)}}{\varepsilon_0 c n_0^2} \]  

where \( \varepsilon_0 \) is the permittivity of free space, \( n_2 \) is the nonlinear index of refraction and \( n_0 \) is the linear refractive index. The material response to an ultrashort pulse and corresponding Kerr nonlinearity depends on the pulse duration. For pulses shorter than 100 fs, the induced dipole moment per unit volume results from an electronic response and for longer pulses, the nonlinear refractive index \( n_2 \) is a result of contributions of electronic and nuclear (Raman) responses [2]. The pulse duration dependence of the nonlinear index of refraction also influences the critical power, as described in the following section.

### 2.2.2 Critical power

The critical power is the power at which the wave front curvature from self-focusing and diffraction cancel. Because both self-focusing and diffraction effects are proportional to the beam diameter, a critical power is defined rather than a critical irradiance. By equating the beam divergence with the Kerr self-focusing, a critical power can be calculated [24].

\[ P_{cr} = \frac{3.77 \lambda_0^2}{8\pi n_0 n_2} \]  

where \( n_0 \) and \( n_2 \) are the linear refractive index and nonlinear refractive index, respectively. The factor 3.77 is valid for beams with a Gaussian spatial distribution; however, coefficients for other distributions have been also reported [23, 25]. The nonlinear index of refraction for femtosecond pulses depends on the duration (Sec. 2.2.1)—pulses less than 50 fs will experience a lower refractive index as compared with 100 fs pulses. For longer duration pulses, the reported nonlinear index of \( 4.7 \cdot 10^{-19} \) cm\(^2\)/W [26] includes electronic as well as atomic and molecular
effects such as Raman, molecular reorientation and effects of Brillouin scattering [27]. For shorter duration femtosecond pulses, the nonlinear index results almost exclusively from the electronic response and therefore the critical power is higher. For a 6.3 fs pulse, the critical power was reported as $18 \pm 1$ GW [28]. As the pulse duration increases, the critical power decreases. For a 43 fs pulse the critical power has been reported as 10 GW with a gradual decrease to 5 GW as the pulse was chirped to 200 fs [29].

2.2.3 Plasma defocusing

A self-focusing beam in air experiences a rapid onset of ionization, as a result of multiphoton processes. Oxygen is ionized first and is followed by nitrogen. The ionization energy ($U$) is 13.6 eV and 14.5 eV for oxygen and nitrogen, respectively. For a pulse at 800 nm (1.5 eV), multiphoton ionization (MPI) (Sec. 3.3.2) of $O_2$ requires 9 photons; therefore, a small change in irradiance results in a significant change in ionization. As the pulse irradiance continues to increase, as a result of self-focusing, tunneling ionization (Sec. 3.3.3) becomes increasingly probable. For ultrashort pulses, plasma generation in air is primarily the result of MPI and tunneling ionization. Because the mean free time for an electron is $\sim 1$ ps, there is insufficient time for significant inverse Bremsstrahlung absorption (Sec. 3.3.1) and optical breakdown to occur on the timescale of the pulse [2].

The underdense plasma is assumed to have an equal number of free electrons and ions. Because the free electrons experience negligible restoring force during their interaction with the incident electromagnetic field, the motion of these free electrons can be described by the Drude model. The resulting refractive index of the plasma can be written as [3]:
\[ n_p \approx n_0 - \frac{e^2 N(r,t)}{m \varepsilon_0 \omega_0^2} \quad (2-4) \]

where \( n_p \) and \( n_0 \) are the plasma and air refractive indices, respectively, \( e \) is charge of an electron, \( N \) is the electron density of the plasma, \( m \) is the electron mass, \( \varepsilon_0 \) is the permittivity of free space and \( \omega_0 \) is the laser frequency.

For filamentation at distances around 1 km, intense beams that are slightly below the ionization threshold for air have been observed—filament like behavior without ionization [13]. These millimeter diameter ‘light-channels’ were estimated to have an irradiance on the order of \( 10^{11} \) W/cm\(^2\). These channels could result from the last part of the evolution of filamentation. In this case, the irradiance decreases to a level below the ionization threshold, and self-focusing balances diffraction for the spatially filtered intense filament core [2].

### 2.3 Characteristics of filaments

Within this section, the filament characteristics important for remote laser ablation based spectroscopy applications will be discussed. The filament plasma density (Sec. 2.3.1) is correlated to the filament irradiance and can serves as a diagnostic of filamentation. It is, however, unlikely that the plasma channel has a significant effect on the ablation of solid materials (CHAPTER 6). The energy contained within a filament (Sec. 2.3.2) and the temporal profile of the filament (Sec. 2.3.3) have significant effects on the filament-induced ablation behavior (CHAPTER 3 and CHAPTER 6), as ablation is related to the irradiance. The length of a filament is an important attribute for stand-off applications of filamentation.
2.3.1 Filament plasma density

The density of free electrons induced by the filament core has been experimentally determined and reported by several groups [14, 30-37]; however, the reported values range from $10^{12}$ cm$^{-3}$ to $10^{18}$ cm$^{-3}$. This discrepancy likely results from differences in the initial pulse duration, the initial focusing power and the generation of either single or multiple filaments [23]. The use of a positive lens to accelerate the onset of filamentation results in stronger focusing power as compared with self-focusing alone, because the increased focusing power must be compensated by a denser plasma. Experimentally, the difference in plasma density of the filament-induced plasma channel was observed by using lenses with different focal lengths (Figure 2-4).

![Figure 2-4. Comparison of the filament-induced plasma emission for two different lens focal lengths: 20 cm lens (top) and 2 m lens (bottom). Using a short focal length lens, the plasma was clearly visible with the laboratory lights switched on; however, this was not the case for the longer focal length case.](image)

The strong dependence of the plasma density on external focusing conditions was first published by Théberge, et al. [34]. They found that the plasma density increased from $10^{15}$ cm$^{-3}$
to $2 \cdot 10^{18}$ cm$^{-3}$ when the focal length was decreased from 380 cm to 10 cm. The plasma density was determined using two different techniques. A 10 × microscope objective was used to image the emission from molecular nitrogen at 391 nm onto an ICCD camera, and based on the strength of this emission the number of nitrogen ions in the plasma was estimated. A second technique determined the plasma density using a longitudinal diffraction setup based on Fraunhofer diffraction that resulted from the phase shift introduced by the plasma. Qualitatively, these results agree with our observations (Figure 2-4).

Two slightly different complementary techniques were used by Tzortzakis, et al. [31] to characterize the temporal evolution of the plasma density within a filament. The first technique was based on electric cross-conductivity [35] and was used for measuring the density on a nanosecond timescale. Here, two electrodes, one with a 1.5 mm hole and the other with an 8 mm hole, were attached to a high voltage supply (2 kV) and a plasma switch was created by splitting off a portion of the beam and creating plasma in the larger hole in the second electrode after a finite time delay (Figure 2-4a). The peak current was determined by measuring the voltage across a load resister and had an exponential decay; however, the dynamics were only valid for pump-probe delay times greater than 2 ns because of the limited response of their power supply electronics and plasma switching gate itself. For measuring plasma density on a sub-nanosecond timescale, they used time-resolved diffractometry (Figure 2-4b). In this case, the plasma channel acted as a diverging lens that changed the far-field image of the probe beam as viewed on a CCD camera. Recombination of electrons with parent ions resulted in a plasma that was short lived. There was an initial 100 ps rapid decay followed by a slower decay over 300 ps. The initial plasma density, extracted from the kinetic profile, was on the order of $10^{17}$ cm$^{-3}$. 
Measurement of the electrical conductivity of the filament-induced plasma channel is an indirect method of determining the plasma density that yields a time averaged quantity. Moreover, this technique is unable to resolve the sub-nanosecond dynamics of the rapidly decaying filament-induced plasma. The pump-probe diffractometry results of Tzortakis, et al. [31] captured the rapid plasma decay, and their results agrees with our recent streak camera measurements of the filament-induced molecular nitrogen emission (Figure 2-6). In this case, the entrance slit of the streak camera was placed at the exit slit of our 0.5 m Czerny-Turner spectrometer and the ultrafast plasma decay of several nitrogen molecular emission bands was investigated.
Interferometry techniques have been used by Yang, *et al.* [38] and Chen, *et al.* [37] to infer average electron densities of $10^{18}$ cm$^{-3}$ and $10^{16}$ cm$^{-3}$, respectively. In the first study, filaments were created using 25 fs pulses focused with a 2 m lens. A portion of the 800 nm beam was frequency doubled and focused through a Wollaston prism and polarizer. By changing the probe pulse delay, the temporal evolution of the electron density was measured and fit to an exponential curve ($n_e = 6.18 \times 10^{18} \exp^{-0.684} \text{ cm}^{-3}$). In the second study, a folded wave-front interferometer was translated parallel to the filamentation axis to map the electron density along the propagation of the filament. The interferometer was illuminated using a spatially filtered optical probe beam that was created by sampling a portion of the main 800 nm beam line. The electron density was determined for a ‘longer’ pulse (120 fs) and ‘shorter’ pulse (40 fs) to show the effects of the molecular contribution to the optical Kerr effect on the resulting plasma density. The maximum electron density was on the order of $10^{16}$ cm$^{-3}$ and was a function of position along the filament.

To summarize and give perspective, the density of the plasma channel left in the wake of a filament decays rapidly and is highly dependent on external focusing conditions. To date, the
plasma density of non-focused filaments has not been sufficiently quantified—all quantification efforts have been made under external focusing conditions. This point is often forgotten when discussing filament applications that utilize the plasma channel at remote distances.

2.3.2 Energy contained within a filament

The filament is composed of a non-diffracting core and a surrounding energy reservoir. The energy reservoir is essential for filamentation, as the energy reservoir allows the filament to reform if the filament becomes blocked [39-41]; however, the opposite is not the case—blocking the energy reservoir will prohibit filamentation [2]. An energy of ~0.75 mJ within the filament was measured by Braun, et al. [5] using grazing incidence reflections from two glass slides and an energy meter. Similarly, 0.7 ~ 1 mJ per filament was measured by Nibbering, et al. one year later [42]. From their simulated results Kosareva, et al. suggested that a 1.4 times reduction in beam diameter would increase the filament bunch energy from 4% to 20% of the initial beam energy [43]. Over a distance of 80 m, the energy in the filament relative to the total beam energy was measured and the ratio did not exceed 7% for input energies between 2.1 mJ and 8.1 mJ [44]. For an initial 120 fs pulse with energies between 1 mJ and 5 mJ, Lange, et al. [45] reported that only 5-10% of the energy was channeled in the filament.

Although only a limited amount of energy can be channeled within a filament, for most applications (Sec. 2.4), the filament irradiance is a more important metric. For example, the irradiance threshold determines the onset of ionization. The nonlinear dependence of the ionization on the irradiance results in clamping of the filament irradiance and provides shot-to-
shot stabilization of the irradiance. Therefore, with a given energy density within a filament, knowledge of the temporal profile, as will be discussed in the next section, becomes crucial.

2.3.3 Temporal profile of filaments

Although it was initially assumed that the pulse duration during filamentation remains constant [5], temporal compression along filament propagation has been observed [46-53] and numerically modeled [54]. In recent years, temporal compression using filaments has generated interest as a robust method of generating few-cycle pulses [49, 50, 55, 56]. Hauri, et al. [49] demonstrated few cycle (5.7 fs) phase-locked pulses (0.38 mJ) generated through the filamentation of 43 fs 0.84 mJ pulses through a noble gas.

The pulse compression of a transform limited pulse requires the generation of new frequencies—the spectrum must broaden. Spectral broadening during filamentation occurs as a result of self-phase modulation (SPM) and is a consequence of the nonlinearity of the medium. A plane wave in space (z) and time (t) can be described by the following function [2]:

\[ E(z, t) = \exp\left(i[\omega_0 t - k z]\right) = \exp\left(i\left[\omega_0 t - \frac{\omega_0 n}{c} z\right]\right) \]  \hspace{1cm} (2-5)

where \( \omega_0 \) is the angular laser frequency. Because the refractive index experienced by the pulse during filamentation is also a function of time, the above expression can be re-written as:

\[ E(z, t) = \exp\left(i\left[\omega_0 t - \frac{\omega_0 n_0}{c} z - \frac{\omega_0 \Delta n(t)}{c} z\right]\right) \]  \hspace{1cm} (2-6)
\[ E(z, t) = \exp \left( i \left[ (\omega_0 t - \frac{\omega_0 n_0}{c} z) + \int_0^t \frac{\partial}{\partial t} \left( -\frac{\omega_0 \Delta n(t)}{c} z \right) dt \right] \right) \] (2-7)

\[ E(z, t) = \exp \left( i \left[ (\omega_0 t - \frac{\omega_0 n_0}{c} z) + \int_0^t (\Delta \omega) dt \right] \right) \] (2-8)

where \( \Delta n(t) \) is given by the combination of nonlinear optical Kerr effect (Sec. 2.2.1) and the plasma itself (Sec. 2.2.3):

\[ \Delta n(t) = n_2 I(t) - \frac{2\pi e^2 N_e(t)}{m_e \omega_0^2} \] (2-9)

and \( \Delta \omega \) is given by:

\[ \Delta \omega = -\frac{\omega_0 z}{c} \frac{\partial [\Delta n(t)]}{\partial t} \] (2-10)

Because the front part of the pulse experiences a neutral gas (on the time scale of the pulse), \( \Delta \omega \) becomes:

\[ \Delta \omega = -\frac{\omega_0 z}{c} \frac{\partial I(\text{front part})}{\partial t} \] (2-11)

The front part of the pulse is increasing in time and broadens towards the red part of the spectrum (stokes shift). In a neutral gas, the backend of the pulse would experience a blue shift; however, the trailing portion of the pulse experiences a partially ionized gas. Therefore, in the case of a time varying plasma density, the plasma contribution to \( \Delta \omega \) becomes:

\[ \Delta \omega = \frac{2\pi z e^2}{m_e \omega_0^2} \frac{\partial N_e(t)}{\partial t} \] (2-12)
Because the ionization that leads to the time varying electron density is related to the pulse irradiance \( (I) \), the tunneling ionization cross-section \( (\omega) \) and the number density of neutral air \( (N_0) \), Equation 2-12 can be expressed as:

\[
\Delta \omega = \frac{2 \pi e^2 N_0 \omega}{m_e \omega_0^2} I^m(t)
\]  

(2-13)

where \( m \) is the empirically determined slope of the ion yield versus laser irradiance [57]. The plasma term contributes to the spectral broadening towards the blue side of the spectrum.

During self-focusing, the most intense portion of the pulse experiences a higher refractive index than the trailing edge of the pulse. This results in self-steepening of the backend of the pulse. Because of this temporal re-shaping, spectral broadening of the trailing portion of the pulse towards the blue end of the spectrum (Equation 2-11) also occurs. This variation in the refractive index can also lead to pulse splitting. Pulse steepening and pulse splitting have been observed by several groups [58-60]. The pulse profile during filamentation was measured using a transient-grating cross-correlation frequency resolved optical gate (TG-XFROG) by Odhner, et al [61]. A sketch of their setup and measured pulse duration is shown in Figure 2-7. In their experiment, two probe pulses were focused to form an intense interference pattern within the focal region that resulted in a plasma grating. The filament was diffracted from the plasma grating and, after compensation for spatial chirp, was sent into a spectrometer. The delay time between filament and induced plasma grating was scanned to create a FROG trace. For initial pulse duration of 50 fs, the pulse was compressed to 17 fs during filamentation.
2.3.4 Length of a filament

Before the initial filamentation experiments in 1995 [5], it was believed that ultrashort pulses are not suited for transmitting laser energy through the atmosphere over any significant distance [23]. The intensity of an ultrashort pulse decreases with propagation because of diffraction as well as group velocity dispersion. The filamentation length ($l_f$) can be defined as the distance over which the beam diameter remains constant and has a clamped irradiance that is sufficient to induce ionization of the medium [5, 23, 62]. The onset of filamentation, along the propagation, can be controlled by adding chirp to prevent early collapse of the beam [63, 64]. In air, the onset of filamentation can be delayed by adding an initial negative chip—the shorter wavelengths come first. The negative chirp pre-compensates for the group velocity dispersion of air. Although the length of an individual filament is limited to several hundred meters by the finite energy consumption and temporal re-shaping (Sec. 2.3.3) along the propagation direction, pre-chirping the pulse allows for the formation of filaments at long distances. By pre-chirping the initial pulses, an irradiance of more than $10^{12}$ W/cm$^2$ after several kilometers has been observed from filamentation in the atmosphere [12]. Rodriguez, et al.[65] have observed the
propagation of ultrashort pulses at a distance of 20 km using a 2 meter astronomical telescope.
The peak irradiance in the core of a filament varies throughout its life cycle (Sec. 2.1), as was observed by monitoring the acoustic emission that is representative of plasma formation [63]. Although the length of filamentation is limited, the use of pre-chirp enables the application of filamentation at distances well beyond the length of the filament. The various applications for filamentation are discussed in the next section (Sec. 2.4).

2.4 Applications of filaments

Filaments enable the long distance propagation of intense laser radiation, consequently enabling applications that are not otherwise possible using conventional laser focusing. The most commonly cited applications in the filamentation literature involve remote sensing; however, as our fundamental understanding of the filamentation process improves, new applications are likely to emerge that exploit this intrinsic ability of remote energy delivery.

2.4.1 White light continuum generation for LIDAR

Light Detection and Ranging (LIDAR) using filament-generated white light continuum has the potential to overcome many of the limitations of conventional LIDAR. Filaments were first applied for white light LIDAR [66, 67] shortly after Braun, et al. [5] observed filamentation in air. This white light continuum is generated during filamentation through self-phase modulation (Sec. 2.3.3) [68, 69], and as a result, the spectral content of the filament broadens to cover the visible and the infrared spectral regions. Spectral broadening that ranged from 230 nm to 4.5 µm has been observed [18, 70, 71]. It was found that a significant portion of the supercontinuum was emitted in the backward direction [1, 72]—advantageous for the LIDAR
applications. Although conventional Differential Absorption LIDAR (DIAL) has already provided parts-per-billion (ppb) sensitivity over several kilometers [73], the white light filament-based LIDAR eliminates the need for wavelength scanning. Therefore, filament based LIDAR allows single-shot acquisition of the entire spectrum and consequently the detection of a wider variety of pollutants. Over the past decade, filament-based LIDAR has been applied for an increasing number of atmospheric sensing applications [16, 66, 74, 75].

2.4.2 Terahertz emission for spectroscopy

Terahertz (THz) emission has been generated from filaments propagating in air, perpendicularly [76] and in the forward direction [19] with respect to the filament. The emission of electromagnetic pulses from filaments was first predicted in 2000/2001 [77] and sub-THz emission was first experimentally demonstrated in 2002 [76]. The model proposed by Cheng, et al.[77] for THz emission from filaments suggested that the filament-induced plasma channel acquired a net dipole moment along the channel as a result of the Lorentz force acting on the free electrons. The oscillation of these electrons at the plasma frequency resulted in the emission of THz. This first model for THz generation was later disputed [78-82] and over the past decade, THz emission from filaments has continued to attract attention in the filamentation literature [78, 82-90] with a transitional-Cherenkov model commonly cited [19, 86]. Filamentation as a source of THz emission has potential for THz spectroscopy applications. Although THz spectroscopy was born in 1988 with the generation and subsequent detection of THz radiation in free space [91, 92], the absorption of THz radiation by atmospheric water vapor has been problematic. In 2010, Zhang’s group reported laser induced THz detection from 10 m [93] using a technique they called Radiation Enhanced Emission of Fluorescence (REEF). As THz spectroscopy
continues to gain momentum the challenges that were once faced with the reproducibility in generation and detection of THz radiation [94] are beginning to be overcome. Recent collaborative work between LPL and Professor Zhang’s group has produced promising results in the area of REEF detection of THz radiation in a counter propagating geometry—a more suitable configuration for remote THz spectroscopy.

2.4.3 Material processing

The unique numerical aperture that is achieved through filamentation makes filaments a potentially useful tool for material processing applications [95]. Irradiance clamping of laser pulses propagating in solids has been shown in the early 1970’s to result in filament-like structures [11]. Focused femtosecond laser pulses have been employed since the middle of the 1990’s for material processing applications such as waveguide writing [96-100] and three dimensional optical storage [101, 102]. Self-guiding of IR femtosecond pulses has been demonstrated in glass [103, 104] and Couairon, et al. [105] have defined two distinct regions of internal sample modification following filamentation: type I involves a permanent refractive index change without modification of the material structure while type II involves structural damage. Type I results from the generation of an electron-hole plasma without sufficient avalanche ionization. The plasma lifetime was measured to be on the order of 150 fs. Type II modification is characteristic of avalanche ionization, and computations suggest that the plasma density approaches 10% of the critical density (Sec. 3.5.3). Professor Mysyrowicz suggested (2012, Private communication) that filamentation can occur in fused silica without permanent sample modification, as the temporary refractive index modification results from changes in the electronic structure of the amorphous material that results in a localized density change. In
summary, filamentation within solids enables new geometries for the confinement of nonlinear absorption as compared with conventional focused femtosecond micromachining.

2.4.4 Guiding of electrical discharge

Although optical effects on the electrical conductivity of materials have been studied since the early days of the laser, the application of lasers for triggering lightning was first proposed in the literature by Ball in 1974 [106]. Laser induced electrical discharges have been demonstrated in the laboratory using nanosecond laser pulses [107, 108]; however, this approach is limited to distances less than 10 m by avalanche ionization and the formation of balls of plasma that become opaque to the laser pulse. Filaments can create 100 m long plasma channels at kilometer distances—a potential advantage in lightning guiding applications. Filament-guided electrical discharges have been demonstrated over several meters in a laboratory setting and field demonstrations have provided promising results [109-112]; however, conclusive evidence of laser guided lightning remains forthcoming. The limited electrical conductivity and rapid temporal evolution of filament-induced plasma channels result in poor efficiency as compared with rocket driven lightning wires. A possible direction for future filament-based lightning guiding experiments involves the collinear propagation of a second (nanosecond, for example) laser pulse to increase the plasma density and extend the plasma lifetime. Review articles on laser lightning control were presented by Diels [112] and more recently by Kasparian and Wolf [113].
2.4.5 Filament induced plasma spectroscopy

Filamentation has great potential for stand-off spectroscopy, enabled by the transmission of high laser irradiance over significant distances. Conventional Laser Induced Breakdown Spectroscopy (LIBS) (CHAPTER 3) utilizing focused pulses is practically limited to stand-off distances of \( \sim 100 \) m \([114, 115]\). A plane wave focused to a diffraction limited spot size of 100 \( \mu m \) (similar to the diameter of a filament) at a distance of 1 km would require focusing optics with an aperture of \( \sim 20 \) meter in diameter—an impractical scenario.

\[
D_{diff} = 2.4 \lambda F_\# \rightarrow \quad D_{optic} = \frac{2.4 (800 \text{ nm})(1 \text{ km})}{100 \mu m} = 19.2 m \quad (2-14)
\]

Filamentation provides a clamped irradiance on the order of \( 10^{13} \) W/cm\(^2\) and enables plasma creation at distances in excess of 600 m \([12, 13]\). Although filamentation has great potential for application to LIBS, limited quantitative experiments have been reported. The crucial parameters for characterizing plasmas, as will be described in Section 3.5.1, are the plasma electron density and temperature. These parameters were reported on by Xu, et al. for filament-induced plasmas and compared with conventional ns-LIBS plasmas \([116]\). The electron density resulting from the filament-induced ablation of lead (20 ns after the pulse) was determined by stark broadening to be \( 8 \cdot 10^{17} \) cm\(^3\), similar to the density commonly found in ns-LIBS plasmas \( \sim 10^{18} \) cm\(^3\). The plasma temperature was determined using a Boltzmann plot to be approximately 6700 K (also 20 ns after the laser pulse) and is significantly less than what has commonly been seen in ns-LIBS lead plasmas \( \sim 13,000 \) K. As will be discussed in CHAPTER 3, the temporal dynamics of fs laser-induced plasmas are significantly different than ns laser-induced plasmas. Within the framework of filament-based LIBS, however, the signal strength is dependent on the electron
number density and the plasma temperature. The strength of the continuum radiation as well as the degree of ionization of the plasma constituents (Sec. 3.6) are also temperature dependent [116].

The relatively low plasma temperature associated with filament-induced plasmas, as compared with ns-LIBS plasmas, increases the probability for molecular emission (Sec. 7.2) and reduces the continuum emission (Sec. 3.6.1) [117]. With less continuum emission, the background signal within filament-induced LIBS spectra results primarily from white light that is backscattered from the sample. The magnitude of this background emission can be controlled by adjusting the distance between the onset of filamentation and the sample [116]. Because of the reduced background, effective non-gated (Sec. 3.6) filament-induced LIBS is possible, as was reported by Liu, et al. [118]. Their characteristic spectrum was detected by accumulating 10 laser-shots and was composed of Al I and Mg II emission lines with a low level of continuum emission within the spectral range of 200-700 nm. Towards the application of filaments for remote LIBS, they calculated a maximum theoretical detection distance of 1.9 km based on an assumed 1/r² radiometric falloff and the criterion that the signal must exceed three times the standard deviation of the background (background acquired with laser turned off).

For stand-off distances up to 90 m, Rohwetter, et al. found that the number of photons that were emitted from a filament-induced plasma remained constant with propagation distance along the filament [63]. The recorded filament-induced LIBS spectra from a copper sample placed at 37 m, 62 m and 90 m were approximately equal after being corrected for the 1/r² radiometric falloff expected from a point source. They predicted that the detection of copper lines from a solid target should be possible at ~1 km range given an improved detection system.
Daigle, et al. [119] have demonstrated remote filament-induced LIBS for ppm-level sensing of micro-droplets in a cloud chamber located up to 70 m from the laser system. The aerosol, with 10 µm mean droplet diameter, was created with an ultrasonic humidifier using de-ionized water with salt added. From an extrapolation of their results, they predicted ppm-level detection up to 1.25 km. The detection of bioaerosols, such as barley, corn and wheat grain dusts using filament-induced LIBS, was reported by Xu, et al. [120]. Promising results for remote analysis were obtained from their laboratory scale experiments, and although these bio samples have similar atomic chemical compositions, differences in elemental abundance and kinetic behavior (Sec. 7.2) of the CN and C$_2$ molecular bands allowed the three materials to be distinguished.

For stand-off spectroscopy at distances beyond 1 km, filament-induced LIBS has the potential to fill a void that no other technique has filled. The studies presented above [63, 118-120] have suggested that detection should be possible from distances greater than 1 km, given a suitable detection system; however, there have not yet been any demonstrations of filament LIBS at distances beyond 90 m. The difficulty in detection of filament-induced LIBS emission from a stand-off distance of 1 km is illustrated by the quantification of the single-shot emission presented in Section. 7.4. An approach for increasing the plasma emission strength would be to engineer of an array of filaments in time and/or space to enhance the emission signal and therefore reduce the detector requirements.

In addition to the potential for stand-off detection using filament-induced LIBS, the inherent intensity clamping associated with filamentation removes the need for sophisticated focusing optics. For this reason, Tzortzakis and Anglos [121] applied filament-induced LIBS to
the analysis of materials that are characteristic of cultural heritage monuments and sculptures such as brass, lead and characteristic stone types such as cement, limestone, red clay, and white marble. Incidentally, these were the first LIBS experiments to utilize UV filaments. The filaments were generated using 5 mJ from an excimer (KrF) oscillator-amplifier system in conjunction with a dye laser that provided 450 fs pulses centered at 248 nm. The initial beam was focused using a 10 m lens and multiple filaments were observed after 5 m. A year later, Mirell et al. [17] compared IR and UV filaments using a Ti-sapphire CPA system and a frequency quadrupled Nd:YAG oscillator-amplifier system where the pulses were compressed using FC72 fluorocarbon Brillouin scattering. They applied both UV and IR filaments for the analysis of ammonium perchlorate and DNT and found that UV filaments produced better spectra than IR filaments.

2.5 Summary

This introductory chapter has provided a brief overview of the physics of filamentation, the basic characteristics and some of the possible applications. The emphasis of this dissertation is on filamentation-based stand-off spectroscopy applications. The following chapter will provide an overview of Laser Induced Breakdown Spectroscopy (LIBS) (CHAPTER 3).

A few closing remarks on the current understanding of filamentation: the simple filamentation model as a balance between self-focusing and plasma defocusing, does not account for potential higher order Kerr effects [122-124] or molecular effects. Molecular excitation within filaments [36, 57] is evident from the molecular emission—the first negative band of N₂ and second positive band of N₂. Population trapping, rotational revival and molecular alignment
were recently studied by Azarm, et al. [125] and filament-induced birefringence has been observed by several groups using optical pump probe experiments [126-128].
CHAPTER 3. LASER INDUCED BREAKDOWN SPECTROSCOPY

3.1 Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a plasma based elemental analysis technique that offers several advantages over other analysis methods [129-131]. LIBS works on practically any material in any state with little or no sample preparation, and it can be used for stand-off analysis. At the heart of LIBS is the laser induced plasma that atomizes and excites the sample constituents, enabling simultaneous sampling and excitation. The relaxation of excited atoms, ions and molecules results in plasma emission that is characteristic of the sample composition. Light emission from the cooling laser plasma is coupled into a spectrometer/detector and elemental (as well as some molecular) information can be obtained from the resulting optical spectrum. A basic LIBS system (Figure 3-1) consists of a pulsed laser, focusing optics, spectrometer, detector and computer.

![Figure 3-1. Basic setup for Laser Induced Breakdown Spectroscopy (LIBS)](image-url)
LIBS has promising analytical capabilities such as simultaneous detection of materials’ elemental constituents in less than a second and with a single laser pulse. LIBS has been recognized as “a future super star” in terms of atomic spectrometric methods by Winefordner, et al. [132]. Furthermore, remote atomic analysis using LIBS is made possible using laser radiation for material sampling and excitation as well as optical detection of the atomic emission spectrum. There are no restrictions on the properties of the samples analyzed using LIBS as opposed to Raman, IR or fluorescence.

3.2 Historical development

The development of LIBS, a form of Atomic Emission Spectroscopy (AES), was born alongside the invention of the laser and there are many parallels between LIBS technology and advances in laser technology [133, 134]. Prior to the invention of the laser and LIBS only 50 years ago, AES can be traced back to 1556 when Georgius Agricola reported that the color of the fumes emitted from ore can yield information about the material composition [135]. Dielectric breakdown of gas at low pressure has been known for more than 100 years [133] and the emission from excited gas has been used to reveal its atomic composition. The methods of electronic excitation (continuous/interrupted d.c., continuous/interrupted a.c., low/medium/high-voltage spark with high self-induction and low/medium/high-voltage spark with L=0) has been shown to affect the reproducibility, analytical sensitivity and limits of detection [136].

The invention of the laser introduced another method of inducing breakdown on the surface of materials and in gases. For electric fields ranging in frequency from d.c. to microwave, an rms voltage on the order of kilovolts per centimeter is required for gas breakdown
at atmospheric pressure [137, 138]; however, at optical frequencies, an electric field strength on
the order of $10^7$ V/cm is required depending on the gas pressure [139]. Therefore, optical
frequency electric fields this intense were not feasible until the laser was invented. The first laser
induced plasma on a solid (carbon) target was reported by Dacey in 1962 [140] on the
unpublished experiments of W.S. Boyle. The first reported optically induced air breakdown was
reported in February of 1963 by Maker, Terhune and Savage at the Third International
Conference on Quantum Electronics in Paris [141]. Air breakdown resulted from 120 mJ pulses
from a Q-switched Ruby laser with 15 ns pulse duration and focused at f/4 (for a 100 µm spot
diameter this would correspond to an irradiance of $\sim 10^{11}$ W/cm$^2$). These authors were studying
optical third harmonic generation, and they noted that the greatest experimental difficulty was
unintentional sample breakdown. This report of air breakdown using a laser has been said to
have created “a sensation” [138]. Shortly after in November 1963, Meyerand and Haught
published optical breakdown in helium and argon gases as a function of pressure [139]. Their
study utilized a Q-switched Ruby laser with 1 Joule in 30 ns pulses that provided a focused
irradiance of $10^{11}$ W/cm$^2$ and corresponding electric field strength of $10^7$ V/cm. The relationship
between laser irradiance and electric field is given by [3]:

$$I = \frac{1}{2} c \epsilon_0 n|E|^2$$

(3-1)

where $c$ is the speed of light, $\epsilon_0$ is the permittivity of free space, $n$ is the refractive index and $E$ is
the laser electric field.

Laser induced emission for spectroscopy was first reported at the International
Conference on Spectroscopy in June of 1962 at the University of Maryland, College Park. In
their invited paper, *Optical Microemission Stimulated by Ruby Maser*, Frederick Brech and Lee Cross reported stimulated excitation of surfaces resulting from focused light energy from a ruby laser [142]. These authors reported that single flash excitation allowed the spectrum to be recorded from metals. The first reported analytical LIBS study was by Debras-Guedon and Liodec in 1963 [143]. They used ~100 µs long pulses from a ~100 J ruby laser at 694.3 nm focused to ~100 µm to obtain an emission spectrum from metallic samples, compacted powders, wires, and enamel plates. A year later, the first time-resolved spectroscopic measurements from laser induced gas breakdown were reported by Litvak and Edwards. In 1969, double-pulsed LIBS was demonstrated as a method of improving the ablation efficiency (first pulse ablates the material and the second pulse causes heating and further excitation) using multiple spikes from a Q-switched ruby laser [144]. In these early years of the laser, LIBS was used by physicists to study the fundamentals of gas breakdown; however, spectrochemists soon recognized the paramount application of direct laser ablation of surfaces leading to excitation and observation of a spark [145].

Other major advances in AES have resulted from detector development. Spectroscopists have used photomultiplier tubes (PMTs) such as the 1P21 manufactured by Radio Corporation of America (RCA) since as early as 1943 [146]. Two-dimensional detectors were film based until the CCD was reported by Boyle and Smith in 1970 [147] for which they received the Nobel prize in 2009.

Application of LIBS to spectrochemical analysis increased in the 1980’s, because of its unique advantages. LIBS was applied for time resolved spectroscopy of aerosols [148], analysis
of metals [149-151], detection of uranium [152], detection of beryllium [153] and double-pulsed analysis of liquids [154]. The number of LIBS publications increased throughout the 1990’s with practical application of LIBS to problems such as monitoring of environmental pollutants [155-158], process control for material processing [159-161] and space exploration [162]. As a result of the growing number of applications, commercial LIBS instrumentation and systems became more common and with increased effort on portability, such as inside a suitcase [163]. Since 2000, there have been biennial international conferences on laser induced breakdown spectroscopy, beginning with LIBS 2000 in Pisa, Italy. The Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (EMSLIBS) and the North American Symposium on Laser Induced Breakdown Spectroscopy (NASLIBS) are biennial conferences in the years in-between international meetings. In the new millennia, there have been an increased number of LIBS studies using double-pulsed techniques, utilizing ultrafast laser systems as well as studies focusing on remote analysis.

### 3.3 Laser induced ionization

The interaction of a high irradiance laser pulse with a solid target, leading to ablation and plasma formation, is complex and results in many nonlinear processes [164, 165]. Mechanisms for laser induced breakdown are dependent on the laser irradiance, wavelength, pulse duration, and sample properties. With known experimental parameters, accurately predicting the amount of mass ablated as well as the temperature and electron number density of the resulting plasma is nontrivial [166]. For a femtosecond pulse, photoionization occurs primarily as a result of multiphoton and tunneling ionization as the pulse duration is too short to generate a significant electron avalanche. In contrast, excitation, ionization and ablation using longer pulse durations
usually includes cascade ionization. Cascade ionization relies on the presence of initial ‘seed’ electrons in the focal region. The mechanism(s) of initial electron generation can be thermionic, photoionization, multiphoton ionization, tunneling ionization or simply a result of sample imperfections that decrease the effective bang-gap energy. Reducing the number of impurities and therefore the probability of having quasi-free electrons within the focal region of the laser can be approximated using a high purity gas. Without the ionization of a few initial electrons, the initial ionization results from multiphoton effects. Using a high purity gas and a 10.6 µm laser an ionization threshold as high as $10^{13}$ W/cm² was observed [167, 168]. This result illustrated the wavelength dependence of multiphoton versus tunneling ionization mechanisms, as further discussed in the following subsections.

3.3.1 Cascade ionization

For cascade ionization, laser energy is absorbed by electron collisions with neutrals through inverse Bremsstrahlung absorption (IB) [169]. Elastic and inelastic electron collisions result in energy loss through the excitation of electronic states in atoms and molecules and the excitation of rotational and vibrational states in molecules. Despite these energy losses and the loss of electrons to recombination, an electron within the field of an intense longer duration laser pulse can acquire sufficient energy (ponderomotive potential) to cause excitation and eventually ionization. Stepwise excitation of neutrals, reducing the energy required for ionization, is more probable than direct ionization of neutrals by plasma electrons [170]. This process leads to an exponential increase in electron concentration (cascade breakdown). For cascade breakdown to occur there must be an initial electron in the focal region of the laser and the electron(s) must gain sufficient energy to ionize the material by impact—energy that exceeds the Fermi energy of
the solid. The initial electron for cascade breakdown can result from impurities that effectively reduce the material’s band-gap. At shorter wavelengths, this initial electron can be generated by direct or multiphoton ionization. However, at longer wavelengths, laser induced breakdown can be sporadic for near-threshold irradiation. Optical breakdown using nanosecond laser pulses generally results in cascade breakdown even when the initial electrons are generated through another process. For sub-picosecond pulses, however, an insufficient number of electrons can be generated during the laser pulse for cascade breakdown. Cascade ionization is practically non-existent for femtosecond ionization of a gas, even at an irradiance of $\sim 10^{13}$ W/cm$^2$ [2]. For ultrashort pulses, multiphoton and tunneling ionization are most important.

3.3.2 Multiphoton ionization

Multiphoton ionization is a process where an atom or molecule simultaneously absorbs enough photons to directly cause photoionization (Figure 3-2). The threshold for multiphoton ionization is proportional to $I^m$, where $I$ is the laser irradiance and $m$ is the number of photons that must be absorbed for ionization to occur. This mechanism is most important for shorter wavelength ($\lambda < 1 \ \mu m$) irradiation because the number of photons required at longer wavelengths (lower photon energy) makes this mechanism improbable.

![Figure 3-2. Multiphoton ionization](image-url)
3.3.3 Tunneling ionization

For a valence electron bound to an atom by Coulomb forces, an intense electric field from a high power laser pulse can deform the potential well and allow the electron to tunnel out of its potential well (Figure 3-3).

Figure 3-3. Tunneling of an electron in a Coulomb potential well

For tunneling to occur with an optical frequency electric field, the period of oscillation $t_0$ must be long enough compared to the time $t_i$ the electron needs to tunnel though the potential before the field reverses. Therefore tunneling ionization is more probable for longer wavelengths—an inverse relationship to multiphoton ionization.

The transition between multiphoton and tunneling ionization can be modeled within the framework developed by Keldysh [171] and is characterized by the following:

$$\gamma = \frac{\omega(2m_eE_g)^{1/2}}{2E_A}$$

(3-2)

where $e$ is the charge of the electron and $m_e$ is the effective electron mass, $E_g$ is the material band-gap, $E_a$ is the amplitude of the laser electric field and $\omega$ is the frequency of the laser field.
Multiphoton ionization is dominant when $\gamma$ is much larger than one and tunneling ionization is dominant when $\gamma$ is much less than one.

3.4 Laser ablation

Laser ablation results from the coupling of laser energy into a material that results in part of the material being removed. The removed mass is in the form of atoms, ions, electrons, molecules, particles and clusters. The material is removed as a result of melting, boiling, vaporization, ionization, sublimation, explosion or erosion [172]. Following laser induced ablation a luminous plasma is formed (Sec 3.5). Laser energy is coupled into the material through the interaction with electrons that results in excitation and ionization (Sec 3.3). Although electron-photon interactions can occur on the timescale of the laser pulse, ionization and ablation mechanisms differ for ultrashort (femtosecond or picosecond) as compared with longer (nanosecond, microsecond or millisecond) laser pulses. The following discussion on laser ablation is, therefore, split into two sections based on the regime of laser interaction—femtosecond or nanosecond laser pulse durations

3.4.1 Nanosecond pulsed laser ablation

Thermal vaporization is the dominant mechanism for ablation within the nanosecond regime at irradiances less than $10^8$ W/cm$^2$; however, at higher irradiances, non-thermal mechanisms (as discussed in the context of fs laser ablation) can also contribute to ablation. For thermal vaporization, there is a well-defined transition of the solid from solid-to-liquid, liquid-to-vapor and vapor-to-plasma [172]. The increase in laser-irradiated sample temperature can be described in 1-dimension by the following heat conduction equation [173-176]:


\[
\frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ \left( \frac{k_{th}}{C_p \rho} \right) \frac{\partial T(x,t)}{\partial x} \right] + \frac{\alpha}{C_p \rho} I(x,t) \tag{3-3}
\]

where \(x\) is the position relative to the sample surface, \(T\) is the temperature inside the sample, \(t\) is time, \(k_{th}\) is the thermal conductivity, \(C_p\) is the heat capacity, \(\alpha\) is the absorption coefficient and \(\rho\) is the mass density. \(I(x,t)\) represents the laser irradiance as a function of time and position. The 1-dimensional expression is reasonable if the laser beam diameter is much larger than the penetration depth.

As the sample surface temperature increases, the vapor pressure become significant. The vapor pressure as a function of sample temperature can be obtained by integrating the Clausius-Clapeyron equation and is given by the following [173]:

\[
P_{vap}(T_s) = p_0 \exp \left[ \frac{\Delta H_{lv}(T_s - T_b)}{RT_s T_b} \right] \tag{3-4}
\]

where \(T_s\) is the sample surface temperature and \(T_b\) is the boiling point at atmospheric pressure, \(H_{lv}\) is the heat of vaporization and \(R\) is the gas constant.

Within the regime of nanosecond laser pulses, coupling between the laser pulse and the resulting plasma is also possible on the timescale of the pulse and is dependent on the density of the plasma and the laser wavelength. This ‘plasma shielding’ can influence the quantity of mass ablated, converted into vapor and the properties of the vapor. The absorption of laser energy by free electrons within the plasma through collisions with atoms and ions results in inverse Bremsstrahlung absorption (Sec 3.6.1). The absorption coefficient for inverse Bremsstrahlung is described by [172]:
\[ \alpha_{IB} = \left[ Q N_e N_0 + \frac{4e^6 \lambda^3 N_e Z^2 N_i}{3hc^2 m_e} \times \left( \frac{2\pi}{3m_e k_B T_e} \right)^{\frac{1}{2}} \right] \times \left[ 1 - \exp \left( -\frac{hc}{\lambda k_B T_e} \right) \right] \]  \tag{3-5} 

where \( Q \) is the photon absorption cross section during electron collision with an atom, \( h \) is Plank’s constant, \( c \) is the speed of light, \( T_e \) is the electron temperature, \( Z \) is the ion charge, and \( N_e, N_0 \) and \( N_i \) are electron, atom and ion number densities, respectively.

With short wavelength (higher photon energy) nanosecond laser pulses, direct bond breaking becomes possible and fragments, clusters, single atoms and/or molecules, can desorb from the sample surface [177].

### 3.4.2 Femtosecond pulsed laser ablation

During the timescale of a femtosecond laser pulse, a large number of electrons can be ejected from the sample surface; however, the lattice remains vibrationally cold. Because there is no mass ablated on this timescale (other than electrons), plasma shielding, as considered for nanosecond laser ablation (Sec 3.4.1), can be neglected. For ultrashort pulses, energy is transferred to the material through the electrons. When energy is deposited such that a sufficient number of electrons become ionized, bond breaking and ablation can result through Coulomb explosion. This electronic mechanism of material removal results from a high degree of photoemission that leaves a positively charged material surface such that Coulomb repulsive forces between ions cause disintegration of the surface [178, 179]. Although Coulomb explosion has been observed for semiconductors and dielectrics, it remains controversial with respect to metals [180, 181]. The electric field generated by the separation of electrons from the lattice is generally insufficient to break the interatomic bonds in metals, as a result of their enhanced
carrier mobility [181]. For femtosecond laser irradiation of metals, a rapid transition from solid to vapor may occur [182-184].

Light absorption in metals occurs primarily through free-free transitions of electrons within the conduction band of the material. Although femtosecond laser-induced thermalization of electrons occurs on a timescale of 10 fs to 1 ps, energy transfer from the electrons to the lattice through electron-phonon coupling is much slower, typically occurring between 1 ps and 100 ps [177]. As the electron and lattice subsystems are in transient non-equilibrium, a two temperature model can be described using the following coupled differential equations [185]:

\[
C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla [k_e(T_e, T) \nabla T_e] - \Gamma_{e-ph}(T_e)[T_e - T] + Q(x, t) \tag{3-6}
\]

and

\[
C(T) \frac{\partial T}{\partial t} = \nabla [k_l(T) \nabla T] + \Gamma_{e-ph}(T_e)[T_e - T] \tag{3-7}
\]

where \(C_e\) and \(C\) are the heat capacities for electron and lattice subsystems per unit volume, respectively. The thermal conductivity of electrons and lattice are represented by \(k_e\) and \(k_l\) respectively. \(Q\) represents the source term, and in 1-dimension, can be re-written as \(Q(z, t) = \alpha A I(t)\exp(-\alpha t)\) and \(\Gamma_{e-ph}\) represents the electron-phonon coupling constant. A solution to these coupled differential equations can only be obtained numerically.
3.5 Laser Induced plasmas

In 1922, Irving Langmuir used the term plasma to describe an ionized gas of electrons, ions and neutrals [186]. Laser induced plasmas have approximately the same number of electrons and ions, and quasi charge-neutrality is maintained because of Coulomb attraction between the electrons and ions; however, electron temperature and electron density are used to characterize these plasmas because electron collisions are more likely than ion collisions.

3.5.1 Plasma temperature and density

To describe the energy within laser plasmas, there are four different types of temperature that correspond to statistical descriptions of the radiative, ionization, excitation and kinetic energies of atoms, ions and electrons. These energies are associated with Planck, Saha, Boltzmann, and Maxwell functions respectively [187]. An effective temperature can be described for each energy distribution, yet complete Thermodynamic Equilibrium (TE) must exist for the same temperature to describe all energy forms. TE and the concept of Local Thermodynamic Equilibrium (LTE) are discussed in the next section. For LIBS plasmas the electron temperature and the electron density are generally used.

Laser induced plasmas used for spectroscopy have a relatively high electron density and low electron temperature. The electron density of LIBS plasmas (~10\(^{18}\) cm\(^{-3}\)) can reach values close to normal air density (~10\(^{19}\) cm\(^{-3}\)). LIBS plasmas generally have a low electron plasma temperature (< 1.7 eV) compared to the ionization energy for most materials (from 3.9 eV for Cs to 24.6 eV for He). Generally, LIBS analysis relies on emission that results from bound-bound transitions of singly ionized or neutral atoms. The relationship between the number density of
ions in their first ionization state and the plasma temperature is given by the Saha-Boltzmann equation [188]:

\[
n_i^2 \approx 2.4 \times 10^{15} n_n T_2^2 \exp \left( - \frac{U_i}{k_b T} \right)
\]  

(3-8)

where \(n_i\) and \(n_n\) are the ion and neutral atom number density (number per cm\(^3\)) respectively, \(T\) is the plasma temperature in Kelvin (assuming thermal equilibrium), \(U_i\) is the ionization potential of the atom and \(k_b\) is Boltzmann’s constant. A more general expression for the ratio of spectrally integrated emissivity can also be obtained by combining the ionization and excitation equations of Saha and Boltzmann, respectively [187]:

\[
\frac{e_{ij}^{ion}}{e_{mn}^{atom}} = \left( \frac{A_{ij}^{ion} g_i^{ion} \lambda_{mn}^{atom}}{\lambda_{mn}^{atom} g_m^{atom} \lambda_{ij}^{ion}} \right) \left( \frac{2(2\pi m_e k_b T)^{3/2}}{N_e h^3} \right) 
\times \exp \left( - \frac{U_i^{ion} - \Delta E_i^{ion} + U_i^{ion} - E_m^{atom}}{kT} \right)
\]  

(3-9)

where \(e\) is the spectrally integrated radiant emissivity, \(A_{ij}\) is the upper level transition probability, \(g_i\) is the upper level statistical weight, \(\lambda\) is the wavelength, \(m_e\) is the electron mass, \(k_b\) is the Boltzmann constant, \(T\) is temperature, \(N_e\) is the plasma electron density, \(h\) is Plank’s constant, \(U_i^{ion}\) is the first ionization potential and, \(\Delta E_i^{ion}\) is the lowering correction parameter.

Laser plasmas with a relatively low degree of ionization have a number density of electrons that is similar to the density of ions. These densities are coupled through the conservation of charge:

\[
N_e = \sum_{z=0}^{q} Z N_i^z
\]  

(3-10)
where $N_e$ and $N_i$ are the electron and ion number densities respectively and $Z$ is the degree of ionization ranging from zero to $q$.

### 3.5.2 Local thermodynamic equilibrium

Thermodynamic equilibrium exists when the four different plasma temperatures (Sec. 3.5.1) are equivalent. Because full thermodynamic equilibrium requires each process to be balanced with its inverse process [189], TE cannot be practically realized (other than a blackbody radiator), and approximations are made. Local Thermodynamic Equilibrium (LTE) can be used to describe plasmas that are homogenous and stationary with significantly greater collisional de-excitation rates than radiative decay rates in the system. The LTE approximation can sometimes be used when characterizing LIBS plasmas even though they are transient and inhomogeneous. The lower limit for plasma electron density under which the LTE approximation can be employed is given by the McWhirter criterion [187]:

$$n_e \geq 1.6 \times 10^{12} T^{1/2} (\Delta E)^3$$

(3-11)

where $T[K]$ is the plasma temperature and $\Delta E[eV]$ is the maximum energy transition under which the condition holds. Although LTE does not exist when the McWhirter criterion is not satisfied, the opposite is not true—satisfaction of the McWhirter criterion does not insure LTE conditions [190]. Because laser plasmas are dynamic in space and time, the validity of the LTE approximation relies upon the observation being temporally sufficient to consider collisional de-excitation, yet short enough that results are not time averaged. Similarly, the spatial temperature dependence should be considered when employing the LTE approximation.
3.5.3 Critical electron density

The electron density of a laser induced plasma decreases with distance from the target. The electron density at which the plasma becomes opaque and reflects incident laser radiation is called the critical electron density. Plasma electrons naturally oscillate at the *electron plasma frequency* that is given by:

\[ \omega_p^2 = \frac{N_e e^2}{m_e \varepsilon_0} \quad (3-12) \]

where \( \omega_p \) is the plasma frequency, \( N_e \) is the electron density, \( m_e \) is the mass of an electron, \( e \) is the charge of an electron and \( \varepsilon_0 \) is the permittivity of free space. At the critical plasma density, the laser frequency and the plasma frequency are equal. The critical plasma density is inversely proportional to laser wavelength squared (Table 3-1).

<table>
<thead>
<tr>
<th>Laser</th>
<th>Wavelength (μm)</th>
<th>( n_c ) (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>10.6</td>
<td>( 10^{19} )</td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>1.06</td>
<td>( 10^{21} )</td>
</tr>
<tr>
<td>Ti:Sapphire</td>
<td>0.80</td>
<td>( 1.5 \cdot 10^{21} )</td>
</tr>
<tr>
<td>Nd:YAG (3(^{rd}) Harmonic)</td>
<td>0.35</td>
<td>( 9 \cdot 10^{21} )</td>
</tr>
<tr>
<td>KrF</td>
<td>0.25</td>
<td>( 1.6 \cdot 10^{22} )</td>
</tr>
</tbody>
</table>
3.6 Radiation from plasmas

The spectral emission from LIBS plasmas provides both qualitative and quantitative information about the concentration of each element in the sample. However, this emission depends on the concentration of each element as well as plasma parameters such as the temperature and electron density. Therefore, the integrated line intensity (photons per unit volume per unit time) can be expressed as [187]:

\[
I_{ij} = \frac{A_{ij} g_i}{U_s(T)} n^s e^{-\frac{E_i}{k_BT}}
\]

where \(A_{ij}\) is the transition probability from upper level \(i\) to lower level \(j\), \(g_i\) is the statistical weight for the upper level, \(n^s\) is the total number density for a particular plasma constituent, \(U_s(T)\) is the internal partition function at a specific temperature, \(E_i\) is the excitation energy of the upper level \(i\), \(k_B\) is the Boltzmann constant and \(T\) is the temperature. This relationship assumes that the plasma can be described within the approximation of local thermodynamic equilibrium.

Figure 3-4. Energy level diagram showing free-free (a), free-bound (b) and bound-bound (c) transition.

Spectral emission from laser induced plasmas consists of atomic and ionic lines (as well as molecular bands) that are superimposed on a broad continuum emission. For a given element,
the characteristic line emission depends on the degree of ionization, which is temperature dependent, as well as the number density of the particular emission species in the plasma. The transient nature of the plasma results in time dependent emission and therefore gated detection of this emission is used for spectroscopy to optimize analytical usefulness (Figure 3-5).

![Figure 3-5. Time dependence of emission from laser plasma](image)

3.6.1 **Continuum emission**

Broad spectral continuum emission is usually observed during the rapid heating of the plasma. This emission is a result of free-free and free-bound interactions as well as Stark broadening, and it is present until after the laser pulse. Bremsstrahlung (from German: *bremsen* meaning ‘to slow down’ and *strahlung* which means ‘radiation’) is the broad spectral emission that results when electrons give up kinetic energy after collisions with ions. Bremsstrahlung emission is labeled ‘free-free’ emission because the electron is free before and after the emission of radiation. The Bremsstrahlung spectrum is characteristic of the electron kinetic energy distribution and is therefore dependent on temperature. The temperature dependence of the emitted power resulting from Bremsstrahlung scales with $T^{1/2}$ (in the case of a Maxwellian
distribution) as compared with \( T^d \) dependence (Stefan-Boltzmann radiation law) of a black body radiator [191].

Recombination of free electrons with ions (free-bound) is another source of continuum emission in plasmas. The characteristic spectrum of recombination emission begins at the ionization potential energy and decreases towards higher photon energies as the electron energy distribution decreases.

3.6.2 Line emission

Laser-induced plasma spectroscopy relies on characteristic spectral lines emitted from excited atoms and ions resulting from radiative transitions. Spectral lines result from an energy change during bound-bound transitions (Figure 3-4 c) and can be emitted or absorbed. Generally, the most useful transitions for spectroscopy are between two excited states—a transition not involving the ground state. Transitions that involve the ground state (resonant transitions) generally have a higher radiative probability; however, these lines are more self-absorbed. Self-absorption can occur when there is a difference in plasma temperature and density between the center and the periphery of the plasma. In this case, the periphery contains mainly ‘colder atoms’ that are more likely to absorb the emission from the plasma core [192].

3.6.3 Line broadening

Broadening of spectral lines is the departure from an infinitely sharp line \( (\Delta E \Delta t \sim \hbar) \), and for laser plasmas broadening typically results from Doppler and pressure broadening [193]. Doppler broadening results from the Maxwellian velocity distribution of emitting species and is
most noticeable at low pressures and assuming optically thin plasma conditions. The Full Width at Half Maximum (FWHM) for a Doppler broadened line is given by:

$$\Delta \lambda_{Doppler} = \lambda_0 \sqrt{\frac{8k_bT \ln(2)}{m_a c^2}} \tag{3-14}$$

where \(\lambda_0\) [m] is the center wavelength, \(k_b\) [J/K] is the Boltzmann constant, \(T\) [K] is the temperature, \(m_a\) [kg] is the atomic mass and \(c\) [m/s] is the speed of light.

Pressure broadening includes collisional broadening, resonance broadening, Van der Waals broadening and Stark broadening. Pressure broadening is caused by interactions between emitters and surrounding particles and is inversely proportional to their separation distance. Resonance broadening scales with distance as \(1/r^3\) and is dependent on oscillator strength. This type of line-broadening results from dipole-dipole interaction between identical particles and results in symmetric broadening without shift in wavelength. Line broadening as a result of the interaction between two neutral particles is described by Van der Waals broadening. Stark broadening results from the perturbation of an emitting atom by the electric field of an electron or ion. For atoms other than hydrogen (linear Stark effect), this effect is proportional to square of the electric field (~ \(E^2\)) and inversely proportional with separation distance (\(1/r^4\)). Stark broadening is accompanied by a shift towards longer wavelength and is given by [194]:

$$\Delta \lambda_{stark width} = 2\left[1 + 5.53 \times 10^{-6} n_e^\frac{1}{3} \alpha \times \left(1 - 0.0068 n_e^\frac{1}{6} T^{-\frac{1}{2}}\right)\right] \times 10^{-22}wn_e \tag{3-15}$$

$$\Delta \lambda_{stark shift} = \left[\frac{d}{w} + 6.32 \times 10^{-6} n_e^\frac{1}{3} \alpha \times \left(1 - 0.0068 n_e^\frac{1}{6} T^{-\frac{1}{2}}\right)\right] \times 10^{-22}wn_e \tag{3-16}$$
where $N_e [m^{-3}]$ is the electron number density, $w [m]$ is the electron impact half width, $d/w$ (dimensionless) is the shift to width ratio, $T[K]$ is the temperature and $\alpha$ is the ion broadening parameter.

Line broadening for typical LIBS plasma has a Lorentzian line shape and is assumed to be primarily the result of Stark broadening with negligible ion broadening. Therefore, Equation 3-15 reduces to [187]:

$$\Delta \lambda_{\text{stark width}} = 2wn_e 10^{-22}$$  \hspace{1cm} (3-17)

With known electron impact half width [195], the electron density can be approximated by measuring the half width of an emission line.
CHAPTER 4. EXPERIMENTAL FACILITIES AND DIAGNOSTICS

4.1 Laser systems

The following sub-sections provide an overview of the two laser-systems that were primarily utilized for the work discussed in this dissertation—a dual-wavelength double-pulse system for LIBS and fs system for filamentation.

4.1.1 Dual-wavelength double-pulse laser system

This double-pulse system consisted of a flash lamp pumped q-switched Nd:YAG laser (Brilliant, Quantel) at 1064 nm and a Transversely Excited Atmospheric (TEA) CO$_2$ laser (Lumonics) at 10.6 µm (Figure 4-1). Both lasers were externally triggered using a pair of digital delay generators (DG-535 and DG-645, Stanford Research Systems) at 0.33 Hz, with the maximum repetition rate limited by the CO$_2$ laser. The pulse energy of the Nd:YAG laser was controllable between 5 mJ and 340 mJ using a λ/2 plate and polarizing beam splitter; therefore the pulse energy could be controlled without adjusting the flash lamp voltage and/or q-switch timing. The fluctuation in laser pulse energy was 1.51 % peak-to-peak (PTP) and 0.44 % root-mean-square (RMS) as measured using a pyroelectric energy meter (QE-25 and SOLO 2, Gentec). The Full Width at Half Maximum (FWHM) pulse duration was 5 ns as measured using a photodiode.
Figure 4-1. Nd:YAG / CO$_2$ double-pulse system

The TEA CO$_2$ laser had an external 1 m half-symmetric resonator with intra-cavity iris for limiting the number of higher order transverse modes and therefore provided a circularly symmetric beam profile as measured using a pyroelectric beam camera (*Pyrocam III*, Spiricon). The pulse energy was adjustable between 70 µJ and 80 mJ using crossed polarizers and had 3.5 % PTP and 0.98 % RMS fluctuations. The pulse duration and profile of the CO$_2$ laser pulse was measured using a multiple-junction photovoltaic detector (*PVM-10.6*, Vigo Systems) with nanosecond response time. The pulse shape consisted of a 100 ns pulse followed by a 1 µs ‘nitrogen tail’ (Figure 5-2).
4.1.2 Femtosecond system

High peak power ultrashort pulses, necessary for filamentation, were generated using a Ti:sapphire Chirped Pulse Amplification (CPA) laser system (Figure 4-2). Femtosecond pulses with sufficient bandwidth (Figure 4-2 inset) to support sub-35 fs pulses were generated by a Ti:sapphire oscillator (*Tsunami*, Spectra Physics). The oscillator was pumped with between 4 W and 5 W from a 532 nm CW diode-pumped frequency-doubled Nd:YVO4 (*Millenia*, Spectra Physics) to provide an output power between 400 mW and 450 mW. The oscillator was actively mode-locked using an acousto-optic modulator set to the round-trip time of the cavity of approximately 75 MHz.

![Figure 4-2. Chirp Pulse Amplification (CPA) femtosecond laser system](image)

The pulse energy from the oscillator was only ~ 6 nJ per pulse. The fs pulse train from the oscillator was temporally stretched to approximately 250 ps (measured using a fast photodiode with 4 GHz oscilloscope) using a Martinez grating stretcher to provide positive dispersion.
(longer wavelengths first) to reduce the pulse power during the amplification process. These ‘stretched’ pulses were used to seed a regenerative amplifier (‘regen’) where the pulse energy was increased by six orders of magnitude (nJ to mJ). The regenerative amplifier utilized a Ti:sapphire crystal pumped from both ends with 10 W (20 W of total pump power) from a 1 kHz Q-switched diode-pumped Nd:YLF (Evolution 30, Spectra Physics). The round-trip time of the regenerative amplifier was approximately 12 ns, similar to the oscillator. Seed pulses were amplified, during (T₁ = 105 ns and T₂ = 262) 13 round-trips. The pulse contrast was 10⁻³ for both pre- and post-pulses. The 3 mJ output of the regenerative amplifier could be either further amplified or sent to the compressor. In the case of further amplification, the regenerative amplifier Pockels cells were triggered at 10 Hz and the output pulses were sent through a double-pass amplifier where the pulse energy was amplified from 3 mJ to between 30 mJ and 40 mJ—before compression. The double-pass amplifier was pumped with a frequency doubled flash lamp pumped Nd:YAG (Quanta Ray, Spectra Physics) with 360 mJ pulse energy. In the case of no further amplification after the regenerative amplifier, the 1 kHz output provided 3 W before compression. The compression was performed using a Tracey grating compressor that provided negative dispersion and therefore reversed the effects of the pulse stretcher. For fine adjustments in the dispersion through the system and to compensate for gain narrowing, an acousto optic programmable dispersion filter (Dazzler, FastLite) was inserted between the oscillator and the stretcher (Figure 4-2). The final system output was either 25 mJ at 10 Hz or 2 mJ at 1 kHz with ~50 fs pulses. The ultrashort pulses were measured using Frequency Resolved Optic Gate (FROG).
4.2 Range facilities

For filamentation studies, two different range facilities were used: a 12 m range in the same laboratory as the laser itself as well as a 50 m range within an adjacent service corridor.

4.2.1 12 m range

The laboratory containing the fs laser system (Sec. 4.1.2) was approximately 15 m long and contained a 3.66 m ‘experiment table’, 6.6 m long optical rail and 1.2 m long ‘test station’ located 12 meters from the laser (Figure 4-3).

![Figure 4-3. Laboratory schematic showing 12 m range facility.](image)

The 3.66 m optical table was attached to the laser table with a heavy-duty table yoke assembly and therefore, only six supports were used for the combined two-table system. This 3.66 m table was used for goniometric measurements of the filament-induced plasma emission (Sec. 4.3.2) because of the required distance on either side of the filament-induced plasma was greater than allowed by the small 1.2 m table. To increase the optical path length between the output of the laser system and the end of the 3.66 m table, to allow distance for self-focusing, an optical delay line was setup on the end of the main laser table. This two-table system had the
capability of being floated; however, the majority of the experiments performed with the fs laser system involving filamentation did not require that the table be floated. The optical rail was convenient for characterizing the effects of filamentation as a function of propagation distance (Sec. 6.2). The small optical table at the end of the laboratory was used for the majority of the filamentation experiments that were performed at a distance between 10 and 12 m from the last turning mirror or from the last focusing optic. Experiments such as: filament-induced ablation (CHAPTER 6), characterization of the filament fluence profile (Sec. 4.5) and shockwave characterization (Sec. 7.2).

![Figure 4-4. Photograph of 6.6 m optical rail within 10 m range](image)

**4.2.2 50 m range**

For longer range filamentation experiments, a service corridor that extended almost the entire length of the CREOL building was used to provide 50 m of propagation distance (Figure
4-5). The beam was sent into the service corridor through a 5 cm diameter hole in the wall that separated the corridor from the laboratory. This hole was about 2.5 m from the output of the laser system. Once in the corridor, the beam was redirected using 2 inch diameter dielectric mirrors mounded on an optical breadboard that was vertically supported by a concrete wall on the opposite side of the corridor with respect to the laser laboratory. A second optical breadboard, that was also vertically supported, was used at the down-range end of the corridor that was approximately 50 m from the laser turning mirrors.

Figure 4-5. Cutaway of CREOL building schematic that shows the location of 50 m indoor range facility.

During the propagation of high peak power laser pulses through this service corridor, both warning signs as well as physical barriers were used to keep unauthorized persons from potential laser exposures. When utilized during normal business hours, laboratory personnel equipped with safety glasses and a portable radio were positioned outside the corridor to further secure the
range facility against unauthorized entry. The majority of the experiments that utilized this service corridor as a laser range were performed during nighttime hours when there were fewer people in the building.

4.3 Spectroscopy setups

4.3.1 Spectral imaging

Spectral imaging experiments were performed using the femtosecond laser system described above (Sec. 4.1.2) operated at a repetition rate of 10 Hz and with pulse energy of 14 mJ per pulse. The sample was a 2 x 3 x 0.25 inch graphite block with rms surface roughness less than 0.4 µm, measured using an interferometric microscope (*NewView 6300*, Zygo), with a purity grade of EC-17 and purchased from the GraphiteStore.com.

A negative lens combined with a positive lens provided an adjustable focal length that was used to initiate filamentation (Figure 4-6). The geometrical focus of this lens combination was near the sample, approximately 4 meters from the lenses. Filamentation was initiated approximately 1 meter in front of the sample. Although the sample was positioned within a sample chamber, these experiments were performed at normal atmospheric pressure and room temperature. Plasma emission was collected at 90° from the laser axis using an f/2 triplet objective (*NT47-613*, Edmund Optics). The light collected was transmitted through a fused silica chamber window and dispersed with a 0.5 m Czerny-Turner spectrometer (*2500i*, Princeton Instruments) with 600 line/mm grating and detected using a 256 x 1024 ICCD camera (*iStar 720*, Andor). In this configuration each grating position provided a spectral window of approximately 80 nm, and at 400 nm the resolution was 0.08 nm.
Figure 4-6. Experimental setup for measuring the filament-induced plasma spectrally, temporally and spatially. In a) the plasma was imaged onto the entrance slit of an imaging spectrometer with a triplet objective (T) and by translating the mirror (M), the image of the plasma was scanned across the spectrometer slit. The signal and background are shown in b) and the reconstructed image is shown in c).

Spectrally resolved images (Figure 4-6c) were obtained by translating the projected plasma image across the entrance slit of the spectrometer (by translating mirror M in Figure 4-6a) and thus provided the spectrum for a slice of the plasma—a line parallel to the sample surface. Full spectral images were obtained by stitching these image-slices together. For each image slice (mirror position) 100 shots were acquired after 10 ‘cleaning shots’.

This method of reconstructing a spectrally resolved image by scanning the image across the spectrometer entrance slit provided several advantages over simply using a band-pass filter in front of an array detector. The use of a grating spectrometer provided sufficient resolution and adequate throughput while also providing wavelength flexibility. The scanning nature of this method, however, restricted its use to multi-shot analysis.
Angular distribution of spectral emission

The characterization of filament-induced plasma emission as a function of the viewing angle of the detection system was performed using the fs system described above (Sec. 4.1.2) operated at 10 Hz with 23.0 ± 0.674 mJ pulse energy. The sample was a double side polished non-doped GaAs (1, 0, 0) wafers (ATX, Inc.). The plasma emission from in the UV-Vis-NIR spectral regions was characterized using a 0.5 m Czerny-Turner spectrometer (2500i, Princeton Instruments) with 600 line/mm grating and a 256 x 1024 ICCD camera (iStar 720, Andor). The characteristic emission spectrum from GaAs (Figure 7-8) showed that the atomic gallium line 403.30 nm was well isolated from neighboring emission lines. Therefore, an 11 nm FWHM band-pass filter centered at 395 nm (FF01-395/11-25, Semrock) allowed the detection of this line while blocking the emission from neighboring emission lines. The intense emission around 800 nm from the laser itself was blocked using a second band-pass filter. The transmission of both filters was characterized using the above mentioned Czerny-Turner spectrometer as well as a Cary spectrophotometer (Cary 500, Varian), and at 403.3 nm the transmission was 85 % and 0.63 % for the 395 nm band-pass and IR blocking filters, respectively. The second, IR blocking filter, was necessary because of the almost 10% transmission of the 395 nm band-pass filter at 800 nm, as compared with 0.1 % transmission of the IR blocking filter. The transmission spectrum of the 395 nm band-pass filter was shifted towards shorter wavelengths by changing the angle of incidence. An angle of 20° shifted the pass-band of the filter away from the 403.3 nm gallium line and allowed for the background signal to be acquired. Using these filters, the now spectrally-resolved plasma emission from GaAs was detected using an imaging ICCD camera (PI MAX II, Princeton Instruments) (Figure 4-7). The camera used a Kodak 1024 × 1024
CCD with 12.8 µm × 12.8 µm pixels and the 18 mm GEN II image intensifier had a P46 phosphor that allowed fast electronic gating. Characterization of the temporal emission dynamics was enabled by the 5 ns switching time of the image intensifier, and the time window for optimal signal-to-noise was determined to be 30-500 ns after the laser pulse. The plasma was imaged onto the ICCD camera using a 1 inch diameter lens with 10 cm focal length and was positioned to provide 4.3 × magnifications. The entire system was mounted on a 18 × 24 inch breadboard attached to a rotation stage, that allowed the system to view the plasma from -90° to 90° relative to the surface normal.

Figure 4-7. System for measuring plasma emission versus detection angle

This system enabled the temporal and spatial integration of the emission from a specific gallium line as a function of the detection angle. To determine the detected energy, the number of detected ‘counts’ on the ICCD camera was calibrated using a 405 nm diode laser and calibrated power meter (XLP12-3S-H2, Gentec). Although the number of counts scaled linearly
with exposure time (Figure 4-8a) within a range of exposure times, doubling the exposure time did not result in twice the number of background subtracted ICCD counts. The calibration was performed using a 25 µs exposure time and an incident power of 133.6 µW and corresponded to \(562.65 \times 10^9\) integrated counts on the camera.

![Figure 4-8. Characterization of ICCD camera: a) exposure and b) gain for a constant input light level.](image)

The ICCD intensifier gain could be set between 0 and 255. Per the manufacturer, a setting of 0 corresponded to 1 count per electron while a gain setting of 255 corresponded to 80 counts per electron; however, the measured response of the camera to changes in gain (Figure 4-8 b) showed that the relative difference between a gain setting of 250 and a gain setting of 1 was approximately 38.

### 4.4 Shockwave imaging

Two different techniques were used for imaging filament-induced shockwaves. For delay times between 0 and 45 ns, relative to the incident filament, a shadowgraph technique was used and for longer delay times, an ICCD camera was used.
4.4.1 Shadowgraph Technique

A portion of the 800 nm fs laser energy was split off the mean beam line and frequency doubled to provide a 400 nm ‘probe’ beam that was used as an ultrafast strobe for imaging the filament-induced plasma shockwaves. Because of the high power in the main 800 nm beam line, the probe beam was the transmitted beam through a thin-film polarizer ($ BK7, 56°, 780-820 \text{ nm}$, Eksma). The main beam (‘pump’) was reflected from this polarizer and was, therefore, minimally influenced by the insertion of this optical element. Using two $\lambda/2$ plate and a second identical beam splitter, the energy in both beam paths was continuously adjustable. The probe beam was propagated from the main laser table to the small 1.2 m $\times$ 1.2 m optical table across the laboratory (Figure 4-3). On the second optical table, the beam was reduced in size by using a positive lens combined with a negative lens and frequency doubled using a 5 mm $\times$ 5 mm $\times$ 0.2 mm type I BBO crystal (Quantum Technology) cut at 27°. The negative lens was placed on a translation stage to allow the effective focal length of the two lens combination to be adjusted. This allowed the intensity of the probe beam to be increased at the plane of the filament-induced plasma. The blue probe beam was delayed in time using an optical delay stage and was incident on the plasma in a direction parallel to the sample surface (Figure 4-9). The filament-induced plasma and the resulting shockwave were imaged using a long working distance 10 $\times$ microscope objective onto a 21 megapixel digital camera ($5D MK II$, Canon). The light emission from the plasma itself was blocked using the same 395 nm band-pass filter discussed above (Sec. 4.3.2).
The timing overlap between the 800 nm pump beam and the 400 nm probe beam was determined using three different methods: a photodiode (DET 210, Thorlabs) and 500 MHz oscilloscope, a fiber coupled fast photodiode (Model 1514, New Focus) with 4 GHz oscilloscope and optically using a second BBO crystal cut at 44.3° for third harmonic generation. In the case of longer delay times, the Thorlabs photodiode and 500 MHz oscilloscope were used.

The relatively large optical paths required to delay the probe beam beyond 45 ns (corresponding to roughly 15 m of propagation distance) made it challenging to measure shockwave expansion at longer delay times. Therefore, an ICCD camera was used to capture the slower shockwave dynamics at later times relative to the laser pulse, as discussed in the following section.
4.4.2 Detection with ICCD camera

For imaging of the filament-induced plasma shockwaves at longer delay times, relative to the laser pulse, an ICCD camera was used to allow electronic delay generation (Figure 4-10). The imaging ICCD camera, discussed previously (Sec. 4.3.2) allowed for the characterization of shockwave dynamics up to a couple of microsecond after the initial plasma formation (Sec. 7.2), as limited by the field-of-view of the optical system.

![Figure 4-10. System for measuring the filament-induced shockwave dynamics at longer delay times. A 45 mm focal length triplet objective (T) images the shockwaves onto the ICCD camera through a 532 band-pass filter (BP).](image)

In this case, the source of the probe beam was a small 532 nm CW laser (GW-05, Suwtech) that was spatially filtered and expanded. To increase the contrast of the shockwave images, the plasma and corresponding shockwave were created within one arm of a Mach-Zehnder interferometer. The shockwaves were imaged onto the ICCD camera using a 45 mm focal length triplet objective (NT47-613, Edmund Optics) through a 10 nm FWHM band-pass filter centered at 532 nm. Because of the minimum gate time of the ICCD camera, on the order of 5 ns FWHM, this method was only used for measuring longer delay time shockwave dynamics.
4.5 Filament profiling

The relative fluence profile of the filament (Figure 4-12) was determined using an imaging system that consisted of a series of glass wedges (Figure 4-11) to incrementally decrease the fluence. The system, designed by Khan Lim, used the wedges arranged at decreasing angles of incidence to progressively attenuate the filament before being imaged by a CCD camera.

Because the reflection coefficient is highly dependent upon the incident polarization, it was important to use a p-polarized input to for maximum attenuation. This dependence on the incident polarization was compounded by the number of wedges that were used and therefore only the relative fluence was accurately determined.

The system was designed to image the 800 nm light from the filament and to block the visible and infrared light that was also generated during filamentation, using an 800 nm dielectric mirror in addition to a band-pass filter.

Figure 4-11. The filament imager 1.
Figure 4-12. Measured non-focused filament fluence profile at a distance of 10 m. The shaded region represents the standard deviation of 29 measurements.
CHAPTER 5. DOUBLE-PULSE LIBS: EMISSION ENHANCEMENT MECHANISMS

5.1 Introduction

Because of its potential for stand-off chemical analysis, Laser Induced Breakdown Spectroscopy (LIBS), as an analytical technique (Sec 3.1), fills a void that no other technique has provided. Compared with mass spectroscopy and other more developed techniques, however, LIBS suffers from laser instabilities (shot-to-shot fluctuations), sample non-homogeneity as well as ablation and plasma irreproducibility, all contributing to a relative standard deviation (RSD) on the order of 5-10 % [196, 197]. Double-pulse LIBS is a technique that was first reported in 1969 [144] and has since been investigated as a method to improve the sensitivity, selectivity and reproducibility of LIBS [144, 197-210]. For stand-off applications of double-pulse LIBS, a collinear geometry has been used [201, 202, 204-207, 209, 210]; however, to better understand the mechanisms for signal enhancement, several groups have investigated an orthogonal geometry [199, 200, 211, 212]. We observed different double-pulse LIBS signal enhancement mechanisms using the same experimental geometry with different samples [209, 210]. Despite the relatively larger number of double-pulse LIBS studies over the past decade, a clear understanding of the phenomena leading to signal enhancement remains the topic of investigation. The possible mechanisms for signal enhancement are the focus of this chapter, and can generally be attributed to one or more of the following effects: laser plasma coupling, sample heating, laser-induced particles or atmospheric effects.

Our research on double-pulsed LIBS utilized the combination of an Nd:YAG laser at the fundamental wavelength of 1064 nm and a CO₂ laser at 10.6 μm. This contrast in laser
wavelengths was chosen because the critical plasma density scales with $1/\lambda^2$ (Sec. 3.5.3). Our original intention was to use the longer wavelength of the CO$_2$ laser to better couple into the plasma created by the Nd:YAG laser. It was expected that laser plasma interaction would occur in the corona of the plasma created by the Nd:YAG laser, further down the density gradient. The longer wavelength radiation would then be absorbed through inverse Bremsstrahlung absorption.

5.2 Laser plasma coupling

Coupling of energy from the second laser pulse into the plasma created by the first laser pulse is most easily observed in the case of orthogonal beam geometries (Figure 5-1a). A reheating configuration exists when the first laser pulse (pulse 1 in Figure 5-1a) is at normal incidence to the sample surface and the second ‘reheating’ pulse (pulse 2 in Figure 5-1a) is incident on the first plasma parallel to the sample surface. In an orthogonal geometry, the second laser pulse can sufficiently intense that a plasma is formed in the air; however, the interaction of the second pulse with the plasma has been reported as being less intense when compared with the interaction of the first laser pulse with the sample [213]. The laser pulse interaction with an already formed plasma has generally presented a moderate increase in the emission line intensity (enhanced limits of detection) as well as an increased plasma temperature [211, 213]. Strong evidence for pulse-plasma coupling has also been reported for collinear dual-pulse LIBS (Figure 5-1b) [160, 201, 202].
In Weidman, et al. [209], we observed moderate emission enhancement using the combination of Nd:YAG and CO$_2$ lasers in a collinear geometry. In this case, the first plasma was created using the Nd:YAG laser at the 1064 nm fundamental wavelength and the plasma was reheated using the CO$_2$ laser (Figure 5-2).

The sample was a polystyrene film ($M_w$ 280,000 dilution of 100 mg/ml in toluene, Sigma Aldrich) spin coated on a silicon wafer with an approximate concentration of 30 µg/cm$^2$. The film thickness was measured with a profilometer (Dektak 150, Veeco) to be 3 ± 0.3 µm. The resulting double-pulse spectrum for polystyrene (Figure 5-3) contained emission lines from atomic carbon (247.86 nm), nitrogen (742.4 nm, 744.2 nm and 746.8 nm), oxygen (777.2 nm,
777.4 nm, and 777.5 nm), molecular emission from the CN violet (0-0) band head (388.34 nm) as well as C₂ Swan band head (516.5 nm). As no order sorting filter was used, the 2nd order of the CN band head was present in the spectra at 776.6 nm. As neither polystyrene nor toluene contain nitrogen, the presence of CN was most likely the result of a plasma phase chemical reaction between carbon from the sample and nitrogen from the surrounding atmosphere, as observed during laser ablation of graphite [214-217] and polymers [214, 218]. A gate delay of 50 ns was used to reduce the background continuum emission and an integration window of 100 µs was used to acquire the complete emission. The purpose of this study was to investigate the signal to noise ratio (SNR) enhancement for the detection of organic materials; therefore, the emission from atomic carbon (2s²2p² ¹S - 2s²2p(²P°)3s ¹P° line at 247.86 nm), C₂ Swan band system (a³Πg - a³Πu, with (0-0) band head at 516.5 nm) and CN violet band system (B²Σ⁺ - X²Σ⁺, with (0-0) band head at 388.3 nm) were primarily considered.

![Figure 5-3. Nd:YAG / CO₂ double-pulse LIBS spectrum from polystyrene [209].](image)
The optimal delay time between Nd:YAG and CO₂ lasers was found to be ~100 ns (Figure 5-4), with the CO₂ laser pulse coming second. The opposite situation (CO₂ laser pulse coming first) resulted in less emission from all three species of interest.

![Figure 5-4. Double-pulse emission intensity versus delay time between laser pulses. Positive time delay corresponds Nd:YAG preceding the CO₂ laser pulse. The opposite situation resulted in less signal from all three emitting species [209].](image)

Using the optimal delay time between Nd:YAG and CO₂ laser pulses of 100 ns, an increased emission signal was observed for double-pulse versus single-pulse irradiation/excitation (Figure 5-5). The enhancement of the line intensity was different for atomic carbon as compared with CN and C₂ molecular emission—a ratio of 230, 20 and 7 for carbon, CN and C₂, respectively. The diameter of the crater in the polystyrene film was approximately constant, and hence constant polystyrene ablated mass, for single and double-pulse irradiation. Therefore, the enhanced emission signal suggested heating of the plasma by the second (CO₂) laser pulse. The greater enhancement for atomic emission versus molecular emission is also consistent with a higher plasma temperature in the double-pulse case, as molecular dissociation increases with temperature. For a higher temperature-plasma we would expect less radical. The
dependence of atomic carbon emission with laser irradiance has been reported as $I^{2.8}$ while molecular emission stayed approximately constant [214].

![Graph showing signal enhancement of carbon, CN and C2 emission lines from polystyrene using double-pulse LIBS. A) Nd:YAG laser and b) Ng:YAG followed by CO2 laser 100 ns later [209].]

SNR was chosen as a figure-of-merit for evaluating the analytical usefulness of the Nd:YAG / CO2 double-pulse LIBS technique. Here SNR can be defined as the peak intensity minus background all divided by the standard deviation of the corrected peak intensity. The uniformity in polystyrene film thickness and concentration allowed sample heterogeneity to be neglected; therefore allowing statistics to be taken over 30 separate shots at 30 separate locations on the sample. The improvement in SNR for double-pulse versus single pulse was 1 to 11 for atomic carbon, 7 to 15 for CN emission and 5.6 to 9.3 for C2 emission.

Although this dual-wavelength double-pulse technique provided noteworthy improvement in the SNR, its added experimental complexity may not justify its use for analytical purposes. Furthermore, it does not resolve the issue of CN radical formation. In terms of better understanding the mechanisms of signal enhancement in double-pulse LIBS, however, this
application of 1.064 µm / 10.6 µm double-pulse LIBS to organic materials has suggested that the second pulse (CO2 pulse in this case) interacts with the plasma created by the first pulse.

5.3 Sample heating

A positive correlation between sample heating and single-pulse LIBS emission has been reported [219-221]; therefore, it is not difficult conceptually to extend this to double-pulse LIBS. In the collinear double-pulse LIBS geometry (Figure 5-1 b), sample heating is practically guaranteed, yet in the orthogonal geometry, the pulse that is orthogonal to the sample (pulse 2 in Figure 5-1a) does not actually interact with the sample directly. In the case of a pre-ablation orthogonal air spark, sample heating was suggested as a possible mechanism for the observed transient signal enhancement [199, 200, 222]. As the pre-ablation air spark generally results in the formation of a plasma between 15,000 K and 20,000 K, heating could result from the absorption of the continuum plasma emission or by transmission of heat through the plasma-generated shockwaves leading to compressive heating [197]. In a recent study, Register, et al. (2012) [223], measured the sample temperature using thermocouples during single- and double-pulse irradiation. They concluded that the measured increase in sample temperature for double-pulse LIBS played only a minor role in the observed enhanced emission signal.

In contrast to our double-pulse LIBS study of organics, Weidman, et al. [209], slightly different enhancement mechanisms were observed when this multi-wavelength double-pulse technique was applied to iron, Weidman, et al. [210]. Iron was used in an attempt to better understand the thermodynamic and spectroscopic properties. With the CO2 laser alone, there was weak emission yet no usable line emission (Figure 5-6b). The greatest signal enhancement
occurred when the CO₂ laser preceded the Nd:YAG (Figure 5-6d)—the opposite situation observed with organic samples (Sec. 5.2).

![Figure 5-6](image)

*Figure 5-6. Comparison between single- and double-pulse spectra of iron: a) Nd:YAG laser only, b) CO₂ laser only, c) double-pulse with Nd:YAG laser preceding the CO₂ laser by 1 µs, d) double-pulse spectra with Nd:YAG laser following the CO₂ laser by 1 µs. In (a), the background is marked by the grey line underneath the spectrum and the stars above several peaks indicate the lines chosen for temperature calculation [210].*

With an iron sample, little if any plasma heating occurred with this Nd:YAG / CO₂ double-pulse technique. The interpulse delay was scanned at least 10 µs in each direction, with either the CO₂ laser preceding the Nd:YAG laser or the Nd:YAG laser preceding CO₂ laser (Figure 5-7).
The maximum signal occurred when the CO\textsubscript{2} laser pulse arrived at the sample 1 μs before the Nd:YAG laser pulse, and at this interpulse delay, an enhancement of approximately 8 × (relative to the Nd:YAG laser alone) was observed. This signal enhancement was accompanied by an increase in the plasma temperature, calculated using the Boltzmann plot technique [134] within the assumption of LTE (Sec. 3.5.2). The parameters that were used for the Boltzmann plot are listed in Table 1. For double-pulse LIBS with the CO\textsubscript{2} laser pulse preceding by 1 μs, the plasma temperature was calculated to be 23,000 ± 2000 K while for single pulse Nd:YAG, the plasma temperature was 15,000 ± 2000 K.
Table 5-1. Parameters used for calculating the plasma temperature using the Boltzmann plot technique [210].

<table>
<thead>
<tr>
<th>Wavelength $\lambda_i$ (nm)</th>
<th>Upper level energy $E_i$ (eV)</th>
<th>Degeneracy $g_i$</th>
<th>Transition probability $A_i$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>268.48</td>
<td>8.43</td>
<td>10</td>
<td>$1.4 \times 10^8$</td>
</tr>
<tr>
<td>269.26</td>
<td>8.37</td>
<td>12</td>
<td>$1.2 \times 10^8$</td>
</tr>
<tr>
<td>270.40</td>
<td>7.97</td>
<td>8</td>
<td>$1.2 \times 10^8$</td>
</tr>
<tr>
<td>271.44</td>
<td>5.55</td>
<td>6</td>
<td>$5.5 \times 10^7$</td>
</tr>
<tr>
<td>273.96</td>
<td>5.51</td>
<td>8</td>
<td>$1.9 \times 10^8$</td>
</tr>
<tr>
<td>274.65</td>
<td>5.59</td>
<td>6</td>
<td>$1.9 \times 10^8$</td>
</tr>
<tr>
<td>274.93</td>
<td>5.55</td>
<td>8</td>
<td>$2.1 \times 10^8$</td>
</tr>
<tr>
<td>275.57</td>
<td>5.49</td>
<td>10</td>
<td>$2.1 \times 10^8$</td>
</tr>
<tr>
<td>278.37</td>
<td>7.70</td>
<td>10</td>
<td>$7.0 \times 10^7$</td>
</tr>
</tbody>
</table>

When the CO$_2$ laser pulse arrived at the sample first, either (i) the CO$_2$ laser pulse heated the sample surface before the arrival of the second pulse or (ii) there was pulse-plasma interaction between the Nd:YAG laser pulse and the weak CO$_2$ laser-induced plasma that likely contained non-excited particle ranging in size from atomic to clusters (Sec. 5.4).
In the case of sample heating, the second laser pulse could have required less energy to melt or vaporize the material, an important factor for above room temperature ablation with relatively long pulse durations. For metals, when the surface temperature increases the reflectivity decrease [224]. Therefore, better coupling of the second pulse could result from either or both of these factors. To better understand the possible effects of sample heating, the heat conduction equation was numerically solved in one-dimension (Figure 5-8):

\[
\frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left( \left( \frac{k_{th}}{c_{p \rho}} \right) \frac{\partial T(x,t)}{\partial x} \right) + \frac{\alpha}{c_{p \rho}} I(x,t)
\]

(3-3)

The parameters used for the numerical model are given in (Table 5-2).
Table 5-2. Values used for (1D) heat equation model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass density, $\rho$</td>
<td>$7.87 \text{ g cm}^{-3}$</td>
</tr>
<tr>
<td>Specific heat, $C_p$</td>
<td>$0.449 \text{ J g K}^{-1}$</td>
</tr>
<tr>
<td>Thermal conductivity, $k$</td>
<td>$0.802 \text{ W cm}^{-1} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>Absorption coefficient, $\alpha$ ($\lambda = 10.6 \mu\text{m}$)</td>
<td>$3.3 \times 10^7 \text{ m}^{-1}$</td>
</tr>
<tr>
<td>Melting point, $T_m$</td>
<td>$1811 \text{ K}$</td>
</tr>
<tr>
<td>Reflectivity, $R$ ($\lambda = 10.6 \mu\text{m}$)</td>
<td>0.967</td>
</tr>
<tr>
<td>Space range</td>
<td>$[x_0 = 0; x_f = 0]$</td>
</tr>
<tr>
<td>Space sampling</td>
<td>701 points</td>
</tr>
<tr>
<td>Time range</td>
<td>$[t_0 = -650 \text{ ns}; t_f = 1849 \text{ ns}]$</td>
</tr>
<tr>
<td>Time sampling</td>
<td>2500 points</td>
</tr>
<tr>
<td>Initial condition</td>
<td>$T(x, t = 0) = 300 \text{ K}$</td>
</tr>
<tr>
<td>Boundary conditions on $x_0$ and $x_f$</td>
<td>$\frac{\partial T(x = x_0, t)}{\partial x} = 0, \frac{\partial T(x = x_f, t)}{\partial x} = 0$</td>
</tr>
</tbody>
</table>
Because the penetration depth of the CO\textsubscript{2} laser radiation into the sample was much less than the interaction diameter (~30 nm skin depth compared to the ~560 \textmu m beam bean diameter), considering problem in one dimension was reasonable. The full beam energy was assumed to contribute to sample heating (source term in Equation 3-3) and therefore, the model does not account for ablation or plasma effects—the full laser energy was assumed to transform into heat. A maximum surface temperature (Figure 5-8) of 860 K was calculated for a time of 550 ns. This suggests that surface melting did not occur on the timescale of the CO\textsubscript{2} laser pulse because the melting temperature for iron is 1811 K. Because the maximum signal enhancement occurred for an interpulse delay of 1 \textmu s, it is unlikely that sample heating was the sole mechanism for signal enhancement. These results are consistent with the recent results reported by Register, \textit{et al.} [223].
5.4 Laser-induced particles

Laser induced material ablation results in the formation particles in addition to the evaporated atoms and ions (CHAPTER 6). These particles can result from the ablation process directly or through condensation in the cooling laser plasma. From an analytical viewpoint, these particles have been seen as a potential source of elemental fractionation (signal not representative of sample stoichiometry) in Laser-Ablation Inductively-Coupled-Plasma Mass-Spectrometry (LA-ICP-MS) [173, 225]. The use of a second laser pulse to further ablate plasma particles and create finer aerosols has been applied as a method of improving precisions in ICP-MS [226]

Continuing the discussion of our dual-pulse LIBS work mentioned above (Sec. 5.3), Weidman, et al. [210], the CO₂ laser produced a bright continuum emission without observed line emission (Figure 5-6b). The temporal profile of this continuum emission overlaid with the calculated surface temperature and the temporal profiles of both laser pulses (Figure 5-9) suggested a strong correlation between plasma emission and surface temperature for the first 700 ns; however, at approximately 1 μs after the arrival of the CO₂ pulse on the sample, the extraction of particles was most likely at a maximum.
The presence of particles in the CO$_2$ laser-induced plume, could have acted a fuel for the second plasma created by the Nd:YAG laser. The interaction of the second laser pulse with nanoparticles within the plasma would be consistent with the timescale of the emission enhancement (Figure 5-7).

5.5 Atmospheric effects

The emission from single-pulse LIBS plasmas depends on the atmospheric gas concentration and pressure [227-229]. A decrease in atmospheric pressure results in an enhanced emission strength until between 5 Torr and 50 Torr and continued reduction of the surrounding pressure causes the signal to decrease. It is not clear if the emission enhancement stems from a reduction in atmospheric number density or pressure. The use of helium as a background gas for LIBS detection of halogens was shown to improve the sensitivity and lower the background noise [230].
In the case of double-pulse LIBS, it was suggested that atmospheric effects may lead to signal enhancements [198]. Based on spatial and temporal emission mapping of femtosecond-nanosecond LIBS in orthogonal pre-ablation spark geometry, it was shown that a pre-ablation spark using a femtosecond pulse could enhance the emission from a second nanosecond pulse well after the femtosecond plasma had decayed. It was also shown that although emission lines originating from the sample were enhanced, emission from atmospheric oxygen and nitrogen were attenuated when compared with single nanosecond pulse ablation. Cristoforetti, et al. [204] studied the effects of ambient gas pressure on collinear double-pulse LIBS. They found a decreased signal enhancement with decreased pressure. Since the plasma expansion was significantly different, they noted that the enhancement factor depended on the detector field-of-view. Expansion of the second laser-induced plasma within the air shockwave created by the first plasma, aiding its formation and expansion, was suggested by Stratis, et al. [200] in 2003 and clearly illustrated by shadowgrams presented by Corsi, et al. [231] three years later.

5.6 Summary

The number of publications detailing the applications of double-pulse LIBS under various experimental configurations has increased since the mid-1990s. Excellent review articles on double-pulse LIBS have been published by J. Scaffidi, M. Angel and D. Cremers [197] and by V. Babushok, F. DeLucia, J. Gottfried, C. Munson and A. Miziolek at ARL [232].

Within the context of this dissertation, these double-pulse LIBS studies have illustrated the importance of laser-material interaction on the resulting plasma dynamics as well as the many complexities associated with applying laser-induced plasmas for spectroscopy. Although laser-
material interaction using ultrashort pulse filamentation constitutes a different regime of interaction, the presented work illustrates the need for fundamental understanding of filament-induced ablation (CHAPTER 6) and filament-induced plasma dynamics (CHAPTER 7), for the application of filamentation for spectroscopy.
CHAPTER 6. ABLATION WITH FILAMENTS

6.1 Introduction

The energy reservoir (Sec. 2.1) plays a crucial role for the propagation of the filament. As a result of this surrounding energy reservoir, filamentation will regenerate if the filament encounters an obstruction; however, when the energy reservoir is obstructed, the filamentation process will be interrupted shortly thereafter [2]. Because the energy reservoir exceeds the modification threshold of some materials, it needs to be considered when discussing filament material interaction. Compared with focused fs irradiation, the filament-material interaction occurs on a similar timescale—before material ejection begins, the pulse has already terminated. In the case of filament ablation, the spatial dynamics of the interaction are different and the atmosphere before the sample is potentially ionized by the filament.

Although the mechanisms for fs pulsed laser ablation discussed previously (Sec. 3.4) remain true for filament-induced ablation, quantitative characterization is an area, unlike focused femtosecond laser-ablation [233], that has received little attention in the literature [95, 234]. This work has focused on this interaction by addressing the following unanswered questions that pertain to filament ablation: how are the quantity and geometry of the altered/ablated material effected by the energy reservoir, as compared with the filament core? How does filament ablation change with position along the filament? How does the ablation change when a focusing lens is used to assist the self-focusing and accelerate the onset of filamentation? How sensitive are the characteristics of filament-induced ablation to changes in the physical and optical
properties of the sample? How does the pointing stability of the filament affect the ablation? What are the effects of multi-shot filament ablation?

Following the filament-material interaction, sample metrology was performed using: optical microscopy (OM), White-light Interferometric Microscopy (WIM) and Scanning Electron Microscopy (SEM). Optical profilometry using the WIM provided nanometer depth resolution; however, the transverse resolution was determined by the numerical aperture of the microscope objective, similar to optical microscopy. Therefore, WIM was used for depth profiling and SEM was used to resolve sub-micron transverse features.

6.1.1 Samples

Four different sample materials were chosen for this work: two semiconductors with significantly different bang-gap energies and two metals with significantly different electron-phonon coupling constants. Although semiconductor wafers provided surfaces 1 ~ 2 nm root-mean-square (RMS) roughness, the surface quality of most bulk metal samples was a significant problem. For example, a solid copper sample with a ‘mirror-like-finish’ from mechanical polishing had an RMS roughness on the order of 50 nm and peak-to-peak (PTP) surface roughness on the order of 200 nm; therefore, it was too rough to investigate single-shot filament-induced ablation. The metal samples utilized were evaporated films that were significantly thicker than the skin depth.
Table 6-1. Optical properties of sample materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive index</th>
<th>Reflection (θ°)</th>
<th>Skin Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>0.08 - j4.56</td>
<td>0.986</td>
<td>28 nm</td>
</tr>
<tr>
<td>Titanium</td>
<td>2.74 - j3.3</td>
<td>0.559</td>
<td>38.6 nm</td>
</tr>
<tr>
<td>Germanium</td>
<td>4.763 - j0.345</td>
<td>0.428</td>
<td>369 nm</td>
</tr>
<tr>
<td>GaAs</td>
<td>3.666 - j0.08</td>
<td>0.33</td>
<td>1.6 µm</td>
</tr>
</tbody>
</table>

Note: Refractive index data 1.6 eV (λ = 775 nm)

6.1.1.1 Semiconductors

Two different semiconductor samples were used: gallium arsenide (GaAs) with a band-gap energy of 1.434 eV and germanium (Ge) with a band-gap energy of 0.67 eV. Both wafers were (1, 0, 0) purchased from (ATX, Inc.). Although, these semiconductors provided a surface with 1~2 nm RMS roughness, they were not immune to surface oxidation within an ambient air atmosphere. Surface oxidation of semiconductors is a well-known phenomenon that results in the formation of a dense native oxide layer typically between 1 nm and 10 nm thick. Oxidation results from adsorption of oxygen to the semiconductor surface and electron transfer as a result of strong electronegativity. Because oxidation occurs at the semiconductor surface, increasing layer thickness requires electron tunneling through the oxide layer and is therefore self-terminating [177]. However, the relatively slow oxidation rates for gallium arsenide [235] and germanium [236] have been previously characterized.
6.1.1.2 Metals

Two different metal samples were used: a transition metal, titanium (Ti) with an electron phonon coupling constant of 0.38, and a noble metal, gold (Au) with an electron phonon coupling constant of 0.17 [237]. The titanium sample was created using e-beam vapor deposition (FC-2000, Temescal) to provide a 1µm thick layer of 99.999% pure Ti on a sapphire substrate, providing a sample with a thickness of 25× the skin depth. The RMS surface roughness was better than 1nm for some samples and as rough as 7~ nm RMS for others. The gold sample was a 500 nm thick layer of 99.99999 % pure Au (17× the skin depth) that was deposited on a sapphire substrate using a thermal evaporator (FL400, Edwards). The RMS surface roughness was 6 nm (Figure 6-25). Noble metals, such as gold, are resistant to oxide formation and although titanium is a transition metal it is also corrosion resistant.

6.2 Constant ablation along the filament length

The diameter and volume of single-shot filament-induced ablation craters remained approximately constant over a propagation distance of 35 m within our 50 m long laser range (Figure 6-1). These ablation results using a gallium arsenide (GaAs) sample were published in Applied Physics Letters, see Weidman, et al. (2012) [234]. The onset of filamentation, after the last beam steering mirror, resulted from self-focusing alone, as no external focusing optics were used and the onset position was controlled by detuning the compressor grating to chirp the initial pulse in time. The initial pulse duration was estimated to be approximately 500 fs (outside the measurable range of our FROG, 20-180 fs) by comparing the propagation distance before the onset of filamentation with the semi-empirical relationship for the distance required for collapse of the beam [23, 238, 239]. The motivation for using GaAs, as the sample material, was three-
fold: (i) characterization of single shot phenomena was possible because of the smooth GaAs wafer surface, (ii) GaAs has been the topic of previous investigations published on the interaction of femtosecond laser radiation with GaAs [240-243], and (iii) the surface oxidation rate has been characterized and considered to be negligible [235].

![Figure 6-1. Single-shot GaAs ablation crater a) diameter and b) volume for propagation distances between 15 and 50 meters. The error-bars represent the standard deviation of 15 single-shot measurements.](image)

The GaAs samples were mounted perpendicular to the filamentation axis and the propagation distances were measured with respect to the last beam steering mirror, which was approximately 5 m from the laser system’s pulse compressor. Metrology of the ablation craters was performed using a white-light interferometric microscope (WIM), profilometer, and optical microscope. The 3.7 % root-mean-square (RMS) and 21.5 % peak-to-peak (PTP) fluctuations in shot-to-shot pulse energy contributed to fluctuation in the onset location of filamentation along the axis as well as fluctuation in the ablation behavior (Figure 6-1). The standard deviation was calculated based on 15 single-shot measurements and is represented by the error bars in Figure 6-1. Although the crater diameter and volume remained quite constant over 35 meters of
propagation, the relative standard deviations (RSDs) were notable. The average crater diameter was 410 µm with 27 % RSD and the average crater volume was 5800 µm³ with 45 % RSD.

A reduction in the shot-to-shot fluctuations (and improved RSDs) in crater diameter and volume as well as a better defined location for the onset and for the discontinuation of filamentation was accomplished using an external focusing optic (Sec. 6.4). In this case, the complete evolution of filamentation was observed (Figure 6-2) within the space constraints of our 12 m laboratory range (Figure 4-3).

![Figure 6-2. Evolution of single-shot filament ablation on GaAs for a beam focused at 10 m. The initial beam had an ellipticity of 1.2, as measured with a beam camera and consequently the resulting ablation craters also presented slight ellipticity, as measured using an optical phase contrast microscope.](image)

In the case of external focusing with a 10 m focusing mirror, the average width was 412 µm with 5.1 % RSD and the average crater volume was 7600 µm³ with 6.8 % RSD (Figure 6-3). Filamentation resulted in constant ablation from 6 m to 11 m with respect to the focusing mirror—beyond the Rayleigh range of approximately 1 m.
The density of GaAs being 5.136 g/cm$^3$ [244], the ablated mass was calculated from the volume of the ablation craters to be about 39 ng and 30 ng for focus-assisted (over a propagation distance of 10 m) and non-focused filamentation (over a propagation distance of 50 m), respectively. This quantity of mass removal is within the usable range required for atomic emission spectroscopy [245], therefore, single shot filament-induced material sampling has potential for chemical analysis at stand-off distances.

The ablation crater diameters for focus-assisted as well as non-focused filamentation regimes were on the order of 400 µm and therefore larger than the filament diameter of 100 µm that is commonly reported in the literature [5, 23]. This result suggests that the energy reservoir also contributed to the ablation of GaAs. The influence of the energy reservoir on the ablation is the topic of the next section (Sec. 6.3).
6.3 Effects of the energy reservoir on the ablation

In order to quantitatively discuss the effects of the energy reservoir on the filament-induced ablation, a precise measurement of spatial profile of the filament was necessary. An imaging system, that attenuated the filament using multiple glass wedges positioned at grazing incidence (Sec. 4.5), enabled the retrieval of a relative fluence profile containing both filament and energy reservoir (Figure 4-11). By comparing the relative fluence profile and the spatial extent of the filament-induced ablation crater, a clear picture of the effects of the energy reservoir on ablation as well as an estimate of the peak fluence were obtained. The ablation threshold fluence for GaAs has been reported for 100 fs pulses to be between 175 mJ/cm\(^2\) and 214 mJ/cm\(^2\) [246, 247]. Similar fluences, at radial distances of a few hundred microns, have been reported using filamentation simulations [248].

For non-focused filamentation within our 12 m range, the onset of filamentation for compressed pulses was approximately 5 m from the last turning mirror (Sec. 4.2.1). Under these experimental conditions, the resulting GaAs ablation crater had an average diameter of 476 µm (Figure 6-4).

Figure 6-4. Single-shot ablation of GaAs with non-focused filaments. The sample was positioned at a distance of 10 m from the last beam steering mirror. A 3D model of the single shot ablation crater (a) and the average profile (b) were determined using WIM. The shaded region (b) represents the standard deviation of 12 single shot ablation crater measurements.
The crater profile for single-shot ablation of GaAs (Figure 6-4) had sharp crater walls, that are characteristic of femtosecond ablation of semiconductors [249], and a raised feature in the center. The raised feature is discussed in Section 6.5. Comparison of the ablation crater dimensions (Figure 6-4) with the measured relative-fluence profile (Filament imaging: Sec. 4.5) provided means for estimating the fluence of the energy reservoir (Figure 6-5).

![Figure 6-5. Comparison between relative filament fluence profile (top) and single-shot GaAs ablation crater (bottom). Shaded regions represent the standard deviation of multiple single-shot measurements.](image)

The spatial extent of the energy reservoir was at least eight times that of the filament core and approached 20 % of the total fluence of the core (Figure 6-5). Assuming an ablation threshold fluence of 195 mJ/cm², based on the above stated values obtained from the literature, the peak fluence was estimated using the average fluence profile (Figure 6-5 solid line) to be 778 mJ/cm². Within the standard deviation of the fluence profile (Figure 6-5 shaded region), the fluence was between 622 mJ/cm² and 934 mJ/cm². Using the initial pulse duration of 50 fs and neglecting pulse shortening, this maximum fluence value of 934 mJ/cm² corresponds to an irradiance of $1.87 \times 10^{13}$ W/cm², within an order of magnitude of the values ($10^{13} \sim 10^{14}$ W/cm²).
commonly reported in the literature [5, 42]. For the case of GaAs, the fluence of the energy reservoir was below the ablation threshold, yet above the threshold for modification, as observed using scanning electron microscopy (SEM) (Sec.6.6).

Using the same experimental conditions as were used for GaAs ablation (Figure 6-4)—the sample positioned 10 m from the laser and ablated using non-focused filaments—single-shot filament ablation of a 1 µm thick titanium film resulted in a crater with similar dimensions (Figure 6-6). The crater walls were again relatively sharp, yet in contrast to GaAs, the maximum crater depth of 70 nm occurred at the center of the crater and the average crater diameter was 560 µm.

![Figure 6-6](image.png)

*Figure 6-6. Single-shot ablation of titanium using non-focused filaments. The sample was positioned at 10 m from the last beam steering mirror. a) 3D model of characteristic ablation crater and b) average crater profile. Both were measured using WIM. The shaded region (b) represents the standard deviation of 7 single-shot ablation crater measurements.*

The larger crater diameter suggests that the ablation threshold for titanium was less than the ablation threshold for GaAs. By comparison of the titanium ablation crater profile with the filament fluence profile (Figure 6-7) the ablation threshold relative to GaAs was about 5 % less—approximately 20 % of the maximum fluence rather than 25 %.
Figure 6-7. Comparison between relative fluence profile of the filament (top) and single-shot titanium ablation crater (bottom). Shaded regions represent the standard deviation of multiple single-shot measurements.

Further discussion of the filament-induced ablation of metals is presented in Section 6.8; however, for the comparison with GaAs, several conclusions can be drawn. Despite a plausible decrease in the ablation threshold for Ti versus GaAs, the depth of the ablation craters was approximately the same—the effective single-shot penetration depth was the same. In the case of Ti, there was no sample modification outside the ablation crater as was observed with GaAs.

Below the ablation threshold, the energy reservoir caused modification to the surface of GaAs, as was observed using optical phase contrast microscopy (Figure 6-2) and SEM (Figure 6-16). This region of discoloration that surrounded the crater was correlated with the propagation distance from the focusing optic (Figure 6-8). Although this region was clearly visible using an optical phase contrast microscope, the surface profile was nearly flat with respect to the unaffected background region, as measured using WIM.
Figure 6-8. Measure of the discoloration which surrounded the GaAs ablation crater, as seen with a phase contrast microscope. Filamentation was assisted using a 10 meter focal length mirror.

This region of sample modification without ablation increased in diameter with propagation distance and likely resulted from sample heating by the energy reservoir, the heat-affected-zone (HAZ). A more detailed investigation of the post ablation-event sample surface was performed using SEM and TEM and discussed in Section 6.6; however, this region of sample modification suggests the following: although the filament core resulted in an almost round ablation crater that remained constant over the length of the filament (Figure 6-3a), sample modification by the energy reservoir more closely followed the focused irradiance profile of the beam.

The significant spatial extent of the energy reservoir, coupled with its near threshold fluence (for GaAs and Ti), becomes important for filament-induced material ablation. The presence of this energy reservoir constitutes one of the greatest differences between focused laser ablation and filament-induced ablation. The transition between focused- and filament-induced irradiation can be seen when a focusing lens is used to accelerate the self-focusing and formation of filaments.
6.4 Effects of external focusing on filament-induced ablation

Although it has become common practice to use a focusing optic to create filaments (of only a couple meters in length) within a laboratory setting, for increased stability and because of laboratory space constraints, filamentation modeling suggests that the fluence profile depends on the initial focusing conditions and that the difference between focused- and non-focused filaments becomes non-negligible at focal lengths shorter than ~5 m [34, 250]. In terms of the effects on material ablation, a noticeable increase was observed in the quantity of mass ablated from a GaAs sample using focus-assisted filaments at a distance of 10 m as compared with self-focused filaments at 50 m (Sec. 6.2).

A more direct comparison between focus-assisted and self-focused filamentation was performed at a distance of 10 m with and without a 10 m focal length lens. Using a focusing lens, the measured relative fluence profile (Experimental setup described in Sec. 4.5) of the filament had approximately the same (FWHM) width as compared with self-focused filaments (Figure 6-9). The average profile widths were 279 µm and 282 µm for focused- and non-focused filaments, respectively. The peak fluence, however, was approximately 1.8 times greater when a 10 m focal length lens was used. Because laser ablation is a highly nonlinear process, this difference in fluence could have a significant effect on filament-induced ablation. The average and standard deviation of these profiles were calculated over 29 single-shot measurements.
Concerning the pointing stability of the filament, an improvement by a factor of two was observed for the case of 10 m lens-assisted filamentation versus non-focused filamentation (Figure 6-10)—improvement of the PTP (RMS) stability from 642 µm (62.5µm) to 310 µm (39 µm) evaluated over 29 single-shot measurements. The spatial instability observed for self-focused filaments resulted from their formation around intensity ‘hot spots’ in the beam.

Figure 6-9. Comparison of the relative fluence profiles for (a) filamentation assisted with 10 m focal length lens and (b) self-focused filamentation.

Figure 6-10. Pointing stability at a distance of 10 m of (a) non-focused filamentation compared with (b) lens-assisted filamentation with.
For filamentation using a 10 m focal length lens, the resulting ablation crater on GaAs was approximately 510 µm in diameter (Figure 6-11) as compared with 476 µm diameter (Figure 6-4), a difference relatively small compared with the diameter. The crater depth in both cases remained approximately constant at 65 nm. Therefore at these well-above-threshold fluence values, the increased fluence in the focus-assisted case had little effect on the maximum depth—saturation of the penetration depth. If the ablation threshold were greater, this difference in peak fluence would likely result in a more significant difference in the ablation behavior.

\[\text{Figure 6-11. The single-shot crater profile for focus-assisted filament ablation. The solid black line represents the average and the shaded region represents the standard deviation over 18 single-shot measurements. The GaAs sample was placed near the focus of a 10 m focal length lens.}\]

The differences between self-focused and focus-assisted filamentation became more pronounced as the lens focal length was decreased. In the case of a 1 m lens, the FWHM of the fluence profile decreased significantly as compared with self-focused filamentation. For the case illustrated here, the laser energy at the focusing lens was 10.2 mJ (2.53 % RMS and 15 % PTP fluctuations), the pulses were compressed to 50 fs and because the experiment was performed at 10 m from the laser, the spatial intensity profile was relatively poor. The width of the filament fluence profile at the onset of filamentation, around 84 cm from the lens, was 303 µm in
diameter, 82 µm in diameter at 93 cm from the lens, and 41 µm in diameter at 97.5 cm and 101.5 cm from the lens (Figure 6-12). The peak fluence increased by approximately by 10× between 84 cm from the lens and 101.5 cm from the lens. From inset (a) within Figure 6-12, rings were observed in the fluence profile. The formation of rings in the transverse profile of a filament created using a 150 cm focal length lens was previously reported by Chin, et al. [251]. Based on numerical simulations, they suggested that these rings result during self-focusing and plasma defocusing.
Figure 6-12. Filamentation with a 1 m focal length lens. As the filament started to form, rings were present in the profile around 84 cm from the lens (inserts a and c). Towards the geometrical focus, the profile developed the appearance of a spatially filtered Gaussian beam. The evolution of the filament between 84 cm and 101.5 cm was compared with Gaussian beam propagation (red dotted line).

Because of this narrowing of the filament fluence profile and increase in peak fluence, as the focal length was decreased, the filament induced air plasma became more intense, and the emission from atmospheric nitrogen ($N_2^+$) became visible by eye.
Ablation of GaAs using the increased filament fluence, enabled through the use of a 1 m focal length lens, better illustrated the dependence of the ablation crater morphology on the filament fluence. The ablation dependence on filament fluence is the topic of the next section.

### 6.5 Fluence dependent ablation efficiency

The cross sectional crater profile for filament ablated GaAs (Figure 6-4) consistently presented a raised central feature—for GaAs, the maximum crater depth was not at the center of the crater. This decrease in the ablation efficiency with fluence was more clearly observed for filamentation assisted using a 1 m focal length lens (Figure 6-13), as the peak fluence was greater. In this case, the GaAs sample was placed 84 cm from the lens and the resulting crater was approximately 486 µm wide with a maximum depth of 65 nm and depth of 35 nm at the center of the crater. Therefore, despite the consistency in the maximum crater depths of 65 nm for both non-focused and 1 m focus-assisted filaments, the increased fluence decreased the ablation depth at the center of the crater.

Figure 6-13. Profile of single-shot GaAs ablation crater resulting from filaments assisted with 1 m focal length lens. The average is shown by the solid line and the shaded region represents the standard deviation of 12 single shot measurements. The sample metrology was performed using WIM.
A decreased ablation efficiency within the central crater region following focused fs laser ablation has been observed by several groups and reported for GaAs [252, 253], silicon [247], indium phosphide [254] and fused silica [27] samples. For focused fs ablation of GaAs, the onset of this decreased-depth phenomenon was observed at a threshold fluence of 1.2 J/cm$^2$ and attributed to surface optical breakdown and high density plasma formation during their 100 fs pulse. For fused silica [27], this decreased ablation efficiency has been observed for pulse durations down to 7 fs and again attributed to the ultrafast, beyond critical density, plasma generation.

Following the filament-induced ablation of GaAs, several forms of ‘post-event’ surface metrology were performed, and the results are discussed in the next section.

### 6.6 Post-ablation surface characterization of GaAs

Surface profilometry of the filament-induced GaAs ablation craters was performed primarily using whitelight interferometric microscopy (WIM). Because WIM can yield false results in the case of spatially varying optical properties of the surface under test, these results were compared with contact profilometry (AlphaStep 200, Tencor) results. For the discussion of filament-induced surface modification, four different regions of the sample surface were identified. These regions are shown in Figure 6-14 by an optical phase contrast image with superimposed depth profile. The different regions of interest, within and surrounding the crater, are the following: i) the central raised feature that was 10 nm to 20 nm higher than the deepest region, ii) the intermediate region between the center of the crater and the crater rim and containing the deepest region that was approximately 60 nm deep relative to the surface, iii) the
ring of discoloration around the crater that was level with the surrounding unaffected background region is depicted by (iv).

Figure 6-14. Filament-induced ablation crater on GaAs at 6.5 meters from the 10 m focal length focusing mirror. The depth profile (shown in white) was measured using WIM and is superimposed on an optical phase contrast microscope image. Four different regions of the crater were identified: i) the central raised feature, ii) the intermediate region between the center of the crater and the crater rim, iii) the ring of discoloration around the crater, and iv) the unaffected background region.

The central region of the crater (region i) was further analyzed using WIM (Figure 6-15) and SEM (Figure 6-16). Although WIM provided sub-nanometer depth resolution, the transverse
resolution was limited by the optical microscope objective—on the order of a micron. Analysis of this region using SEM showed submicron surface features in this region (Figure 6-16).

Despite the presence of micron and submicron particles within the central crater region of filament-irradiated GaAs, the aspect ratio of the raised central feature (Figure 6-14) was not visible using SEM. The spherical shape of the surface particles suggests the formation through re-condensation of ablated material. The central region of the crater had micron size particles while near the rim, the average particle size was less than a micron (Figure 6-16). Although not resolved using WIM, the crater rim was approximately 150 nm thick.

Figure 6-15. Surface profile of the central crater region using WIM.
Figure 6-16. SEM images of a self-focused filament-induced ablation crater on GaAs. An overview of the crater is shown in (a) and zoomed-in views of the center of the crater and the edge of the crater are shown in (b-d) and (e-g), respectively. The apparent ellipticity of the crater results from sample tilt in the SEM.

Surrounding the crater and well beyond the crater rim (Figure 6-14 transition between regions iii and iv), the transition between modified and non-modified regions was observed using
SEM (Figure 6-17). This transition corresponded to cracks in the oxide layer and moving towards the center of the crater, increased patches of apparent surface oxidation was observed.

The central crater region had a significantly thicker (approximately 10 times) amorphous layer as compared with the surrounding regions, as was evident through Transmission Electron Microscopy (TEM) analysis (Figure 6-14). The four regions of the crater identified previously (Figure 6-14) were sampled using a Focused Ion Beam (FIB) to cut-out and isolate the individual regions for analysis using TEM. Representative TEM images of these four regions showing the interface between the crystalline bulk GaAs and an amorphous surface layer are shown in Figure 6-18. The amorphous layer was approximately 50 nm thick in region i, 5-10 nm thick in region ii and approximately 5 nm thick in regions iii and iv.
Figure 6-18. Representative TEM images showing the interface between crystalline bulk GaAs and an amorphous surface layer. The periodicity of the crystalline GaAs is shown in the bottom of the image while lack of periodicity indicates that the material has become amorphous. The black region on the top of the images is a protective layer deposited during FIB cutting of the sample.

The above TEM surface analysis of filament-irradiated GaAs has shown that the thickness of amorphous material was greater within the central crater region—the central region that was raised with respect to the deepest crater region. This spatial dependence in the filament-
induced amorphous layer could provide an alternate explanation for the raised central feature discussed in Section 6.5—the laser-induced amorphous region could have resulted in the physical expansion of this region with respect to the surrounding crystalline regions.

To further analyze the formation of surface particles (Figure 6-16) on GaAs, Electron Energy Loss Spectroscopy (EELS) of the central region of the crater (Figure 6-14 region i) was used to investigate the composition. The particle analyzed was determined to be enriched in gallium and surrounded by a thin layer of arsenic. The concentration is indicated by the brightness of the image. There was a slight amount of residual oxygen present on the sample, possibly adsorbed to the surface between the ablation and TEM/EELS analysis. All three elements are shown superimposed using an RGB color map (Figure 6-19). The presence of Ga islands was observed previously by Boroviec, et al. [255]; however, in contrast to their work using EDX point analysis, we observed an enhanced As surface concentration using EELS (Figure 6-19). The enhanced Ga concentration of a surface particle within the central region of GaAs ablation crater further supports the formation of these submicron particles (Figure 6-16) through re-condensation or melting. The melting points for gallium and arsenic are 29.7° C and 817° C, respectively, and their molten densities are 6.08 g/cm³ and 5.22 g/cm³, respectively [244].
In addition the results using a GaAs sample, the formation of nanoparticles from several other materials was observed, following filament-induced ablation. The indirect observation of particle formation was investigated using ‘witness plates’ as well as the observation of particles on the target material itself.
6.7 Post event characterization of ablation byproducts,

The use of ‘witness plates’, in the vicinity of the ablated sample, provided further information on the formation of nanoparticles. A silicon wafer was placed between 3 mm and 5 mm from the ablated sample to collect particulate matter that was ejected during the ablation process. For filament ablation of metals such as iron and aluminum, the spherical nature of the captured submicron size particles, suggests the possible formation through re-condensation of ablation products. The silicon witness plates were analyzed using SEM (Figure 6-20).

![SEM images and EDS spectra](image)

*Figure 6-20. SEM images (top) and corresponding EDS spectra (bottom) of submicron particles captured using witness plates placed 3-5 mm away from filament induced iron (left) and aluminum (right) plasmas.*

In contrast to GaAs (Figure 6-16), filament-induced ablation of germanium (Ge) resulted in a greater density of nanoparticles within the ablation crater (Figure 6-21). The band-gap of these two semiconductors is significantly different (1.424 eV for GaAs and 0.67 eV for Ge);
therefore, linear absorption in Ge extends further towards the infrared. The density as well as the size of nanometer and micrometer particles decreased with radial distance from the center of the non-focused filament-induced ablation crater on Ge (Figure 6-21a-h), as seen with SEM. Within the central 20 µm region of the crater, a relatively high density of spherical particles on the order of 400 nm in diameter was observed.

Figure 6-21. SEM images showing the density of nanoparticles on the surface of filament-ablated Ge as a function of radial distance from the center of the crater: a) crater overview, b) zoomed-in view of the central crater region, c-h) 0.7 × 1 µm images of nanometer size surface features as a function of radial position
Within the central crater region on Ge, the aggregation of particles (Figure 6-21b) resulted in a raised central feature within the Ge crater profile (Figure 6-22), as observed using WIM and confirmed using contact profilometry. The resulting Ge crater (Figure 6-22) was significantly shallower than was observed for GaAs (Figure 6-4). This likely resulted from differences in the material properties, affecting the absorption of the filament, as well as different resulting plasma temperatures that led to differences in nanoparticle formation. These differences in the filament-induced plasma and resulting shockwave expansion for GaAs and Ge samples are discussed in the next chapter (Sec. 7.2).

![Figure 6-22](image_url)

*Figure 6-22. Non-focused filament-induced ablation crater on Ge measured using WIM. The shaded region represents the standard deviation evaluated over 10 single-shot measurement.*

### 6.8 Ablation of metals: the dependence on physical and optical material properties.

#### 6.8.1 Titanium

Two different titanium samples (Ti # 1 and Ti # 2) were fabricated using e-beam vapor deposition (*FC-2000*, Temescal). The first sample was deposited in the fall of 2011 and the second was deposited in the spring of 2012. Although the same deposition tool was used for both samples and they both consisted of a 1µm thick layer of 99.999% pure titanium, to rule out the
presence of contaminants or other differences in their compositions, the samples were checked using Energy Dispersive Spectroscopy (EDS). The resulting ablation crater for Ti #1 was shown previously (Figure 6-6). In contrast to these earlier results, the ablation profile was significantly different for Ti # 2, the second titanium sample (Figure 6-23). It should be noted that Ti# 1 was ablated using non-focused filaments at a distance of 10 m from the laser while Ti # 2 was ablated using filaments assisted with 10 m lens; however, as discussed in Section 6.4, this difference is not expected to have a significant impact on the ablation properties.

![Figure 6-23. Single-shot filament-induced ablation crater on a 1 μm think titanium later on Al₂O₃ substrate. WIM was used for a) 3D model of ablation crater and b) the average and standard deviation of the crater profile evaluated over 19 single-shot measurements.](image)

Surface analysis of both samples using SEM showed that the non-ablated surfaces were different (Figure 6-24 a and f). The larger feature size observed for Ti # 2 could have been the result of an increased rate at which the second sample was deposited. The smaller feature size observed for Ti # 1 suggests that the titanium layer was denser than the second sample.
Similar to the case of Ge ablation (Figure 6-21) relative to GaAs ablation (Figure 6-16), the size and density of nanoparticles (Figure 6-24) as well as the ablation crater profile (Figure 6-23) of Ti #2 relative to Ti # 1 were significantly different. The aggregation of nanoparticles within the central region of the crater was likely the reason for the raised central feature observed using WIM (Figure 6-23b). As with GaAs (Figure 6-14), four different sample regions were identified and compared (Figure 6-24): non-ablated sample region (a and f), an overview of the ablation crater (b and g), the central region of the crater (c and h), an intermediate region in between the center and edge of the crater (d and i), and region of modification surrounding the crater (e and j) that appeared as a ring of discoloration in both SEM and optical images of the crater. The surrounding ring (Figure 6-24 e and j) was similar for both samples and had the appearance of having been melted.
Figure 6-24. Comparison of two different titanium samples before and after filament-induced ablation.
The analysis of the Ti ablation craters using EDS showed the presence of nitrogen on the surface; however, the concentration was, within the margins of error, spatially uniform across the crater and surrounding matrix.

Despite similar material composition, the physical differences observed using SEM, resulted in different ablation characteristics for these two titanium samples. These observed differences in the ablation behavior of titanium likely affected the resulting plasma emission and expansion dynamics as well as the plasma density and temperature. Therefore, the correlation between these physical sample properties and filament-induced ablation clearly illustrates the complexity of the ablation process and potential challenges for laser-ablation based spectroscopy techniques.

Differences in the material’s optical properties are as important as the material’s physical properties, when discussing ablation behavior. This is illustrated in the next section using a gold sample.

6.8.2 Gold

As compared with titanium, there are several differences in the properties of gold that are worth mentioning: gold is a noble metal with a completely filled d-band (5d^{10}6s^{1}) electron configuration, while in the case of titanium, the d-band is only partially filled (3d^{2}4s^{2}); The electron-phonon coupling constant is less than half that of titanium, 0.17 versus 0.38 (see Ref. [237] and references contained therein). For a wavelength of 800 nm, the reflectivity of gold is almost twice that of titanium (Table 3-1).
In 1999, Wellershoff, *et al.* [256] used the two-temperature model (Sec. 3.4.2) to describe their observed linear dependence (up to nearly 500 nm) of the melting fluence threshold on the thickness of a gold film. Based on these results, they suggested that femtosecond laser-induced damage of metals is thermally driven. Using the two-temperature model, they were able to show the temperature dynamics for both the electron and lattice sub-systems for Au and Ni films. Gold, as an example of a noble metal, showed a much slower transfer of energy between electron and lattice sub-systems as compared with nickel, a transition metal. Because of this slow decay in electron temperature, these hot electrons penetrated into the material well beyond the skin depth at velocities around $10^6$ m/s [257-259]; therefore, the temperature of the backside of a 100 nm thick gold film closely tracked that of the front surface. In the case of a nickel film, however, there was a significant temperature difference between the front and back film surfaces [256].

The gold sample used in this work was deposited using a thermal evaporator and was 99.99999% pure gold. The resulting surface had an RMS (PTP) roughness of 6 nm (28 nm) (Figure 6-26).

*Figure 6-25. Surface profile of a 500 nm thick gold film measured using WIM. The surface roughness was 28 nm PTP and 6 nm RMS.*
The 500 nm thick gold layer deposited on a sapphire substrate was observed to have reflected the filament, and no ablation was observed (Figure 6-25)—the filament fluence did not exceed the material damage threshold.

![SEM analysis of 500 nm thick gold layer on a sapphire substrate following filament irradiation. Insert shows zoomed-in view.](image)

*Figure 6-26. SEM analysis of 500 nm thick gold layer on a sapphire substrate following filament irradiation. Insert shows zoomed-in view.*

With the gold sample mounted at 45° to the incident filament axis, the reflected beam had sufficient irradiance to ablate a GaAs target. This application of the gold sample as a ‘filament mirror’ was demonstrated for the case of a non-focused filament at a position of 45 m from the last beam steering optic (Figure 6-27)
Gold is a commonly used material because of its high reflectivity in the infrared and has been the subject of many investigations. For example, the ultrashort-pulse damage of gold coated compressor gratings, commonly used in CPA laser systems, was investigated by Stuart, et al. [260] using a 1053 nm 300 fs laser system. The multi-shot fluence threshold was about 0.6 J/cm² for a 500 nm thick gold coated mirror that was irradiated at normal incidence. Modeling work by Bulgakova, et al. suggested that melting of a 1 µm thick gold film would occur for an incident fluence of 0.93 J/cm² [181]. Lin, et al. suggested a temperature dependence of the electron heat capacity and electron-phonon coupling for both Ti and Au, based on modeling results [237]. Hwang, et al. observed the formation of nanostructure-covered large scale waves (NC-LSWs) on
a gold foil irradiated with tens of pulses from an 800 nm 65 fs laser with a focused fluence of 0.53 J/cm² [261]. Korte, et al. (2004) observed the formation of nanojets and micro-bubbles on a 60 nm thick gold film fabricated using magnetron sputtering. The bump-like structures occurred for fluences above 0.5 J/cm² and jet-like feature were observed for fluences above 1.1 J/cm² [262, 263]. They suggested that formation of these features was possible because of the slow increase in lattice temperature that corresponded to a longer lasting molten stage. Their results were later modeled by Meshcheryakov and Bulgakova who found that these nano-structures were unique to gold because of properties such as yield stress and the elastic characteristics [264].

For filaments incident on gold, the lack of observed modification (Figure 6-27) was consistent with below threshold irradiation. The estimated peak filament fluence, in the range of 622 - 934 mJ/cm² (Figure 6-5), was within the range of threshold values reported in the literature for fs laser ablation of gold. The high purity (99.99999 %) and high degree of surface smoothness (RMS roughness of 6 nm) of the gold sample used in this work was likely superior to what has commonly been reported in the literature. In contrast to focused fs melting and/or ablation of gold, the larger diameter fluence profile associated with a non-focused filament (Figure 6-7) corresponded to a weaker fluence gradient—potentially advantageous for avoiding filament-induced damage.

Until now, the focus of the work presented in this chapter has been on single shot filament-induced phenomena; however, the repeated irradiation, up to several tens of shots, in the same
location on the gold surface was also unsuccessful in causing noticeable modification. The effects of multi-shot filament-induced irradiation are presented in the next section.

6.9 Multiple shot irradiation: formation of periodic structures

The work described in this section on the effects of multi-shot filament-induced ablation on both Ti and GaAs was investigated in collaboration with the Army Research Laboratory (ARL) at Aberdeen Proving Ground (APG). The ARL and UCF (Sec. 4.1.2) femtosecond laser systems were similar in architecture; however, the pulse durations were different, 100 fs at ARL and 50 fs at UCF.

6.9.1 Characterization of filamentation by ARL fs laser system.

Using the ARL fs laser system, the relative filament fluence profile and pointing stability were recorded (Figure 6-28 a and b) and compared with those observed at UCF (Figure 6-5 and Figure 6-10). It should be noted that the ‘intensity’, given in arbitrary units in Figure 6-28, should not be directly compared with the values obtained at UCF, as the system was extremely sensitive to orientation relative to the laser polarization. From the relative fluence-profile, the relative strength of the energy reservoir was slightly greater than 20 % and the FWHM was 215 µm. The PTP and RMS pointing stability evaluated over 42 single shot measurements were 559 µm and 29 µm, respectively. In comparison, the relative strength of the energy reservoir was greater, the FWHM was slightly less, and the pointing stability was superior, at ARL versus UCF.
Figure 6-28. Measured relative-fluence profile (a) and pointing stability (b), for non-focused filamentation at 10.4 m. The solid line and shaded region represent the average and standard deviation evaluated over 42 single-shot measurements.

6.9.2 Gallium arsenide (GaAs)

For correlation with the work from UCF (Figure 6-4), GaAs was ablated using single-shot non-focused filaments at a distance of 10.4 m (Figure 6-29). Although the crater depths were similar, the crater width was slightly greater using the ARL system—consistent with ablation using a more intense energy reservoir. Post-event crater analysis was performed using WIM.

Figure 6-29. Single-shot non-focused filament ablation of GaAs at a distance of 10.4 m. The solid line and shaded region represent the average and standard deviation evaluated over 19 single-shot measurements.
Filaments suffer from a relatively poor pointing stability (Sec. 6.4), and therefore, a decreased precision when used for multi-shot ablation. For applications such as ablation based plasma spectroscopy, a more important consideration is the quantity of ablated mass (Sec. 6.2). The volume of non-focused filament-induced ablation craters on GaAs began to deviate from the expected linear relationship with an increasing number of pulses (Figure 6-30). The volume versus number of pulses was better fit to the form of a cubic function, for this limited number of pulses. In the case of single-shot filament ablation of GaAs (Figure 6-29), the ablation crater aspect ratio (ratio of width to height) was on the order of 8600:1; therefore, it is unlikely that the geometry of the crater, by itself, would affect the ablation rate for a relatively small number of pulses.

![Figure 6-30. GaAs ablation crater volume versus number of shots. Irradiated with non-focused filaments at a distance of 10.4 m.](image)

Roughening of the surface within the crater, however, would increase the effective surface area and could potentially decrease the ablation rate. Changes of the optical and/or thermal properties of the surface could occur through surface carbonization, corresponding to a
decreased coupling of the laser into the material [177]. The dependence of the ablation volume versus number of pulses, however, was more linear in the case of titanium, as discussed in the next section.

6.9.3 Titanium (Ti)

The titanium sample was created using e-beam vapor deposition to create a 1µm thick layer of titanium on a sapphire substrate. The sample was created within the same deposition run as ‘Ti sample # 2’ that was discussed previously (Sec. 6.8.1). Similar to GaAs, there were slight differences in the single-shot ablation crater profile (Figure 6-31), as compared with previous work (Figure 6-23)—here, the Ti ablation crater had a larger diameter and was deeper.

![Figure 6-31. Single-shot non-focused filament ablation of titanium at a distance of 10.4 m. The solid line and shaded region represent the average and standard deviation evaluated over 18 single-shot measurements. Metrology performed using WIM.](image)

In contrast to the results for GaAs ablation versus number of pulses (Figure 6-30), the ablation crater volume versus number of pulses for Ti was linear (Figure 6-32) up to 50 shots. For ablation using 100 shots, the 1 µm thick Ti layer was ablated through to the sapphire substrate. The raised feature within the center of the ablation crater, observed for the case of
single-shot Ti ablation (Figure 6-31), was the result of a cluster of nanoparticles. The relative height of this raised feature decreased with an increasing number of pulses.

![Graph showing titanium ablation crater volume versus number of shots]

*Figure 6-32. Titanium ablation crater volume versus number of shots. Irradiated with non-focused filaments at a distance of 10.4 m.*

Morphology of the crater surface was observed to be dependent on the number of shots, with the formation of periodic structures occurring after only a few shots. The formation of these periodic structures is the topic of the next section.

6.9.4 Filament-induced periodic structures

Since the mid-1960s, it has been known that multi-shot laser irradiation of solid materials can result in the formation of periodic surface features [265]. There has been an increasing interest in laser-induced periodic surface structures (LIPSS) using both nanosecond laser irradiation [266-270] and, in recent decades, femtosecond laser irradiation [271-279]. In 2005, Rohwetter, *et al.* [63] observed LIPSS on the surface of a bulk copper sample that was ablated at a distance of 90 m using filaments. Although not mentioned in their publication, it is assumed that the observed sub-wavelength ripple pattern resulted from multiple shots as well as multiple
filaments. Despite the observed ripple features created with filaments, the authors noted that under focused irradiation conditions, at 25 m from the laser, no ripples were observed. The dependence of focused fs laser fluence on LIPSS formation was reported in 2010 by Okamuro, et al. for several different metals [280]. A material-dependent fluence range was observed for the formation of LIPSS, therefore providing an explanation for a lack of observed LIPSS on Copper. The difference in LIPSS contrast for Cu, Ag and Au samples was explained by the difference in the electron-phonon coupling constants [281].

The near-threshold fluence within the filament’s energy reservoir potentially created the ideal irradiation conditions for the formation of LIPSS. The multi-shot filament-induced ablation of titanium (Sec. 6.9.3) resulted in the clear formation of LIPSS after ten shots and evidence of increased periodicity after only 5 shots (Figure 6-33). The formation of LIPSS occurred orthogonal to the laser polarization direction, consistent with the majority of low spatial frequency LIPSS reported in the literature. The observed LIPSS period was approximately 0.52 µm, and was within the range of what has been published for focused fs LIPSS on titanium [275, 280, 282].
The formation of LIPSS during filament-induced ablation of titanium (Figure 6-33) has little apparent effect on the ablation rate (Figure 6-32); however, this modification of the material’s optical properties results in an increased surface-to-mass ratio that could become crucial for other applications.

6.10 Conclusion

Motivated in part by the difficulties in quantifying the characteristics of a filament, such as the spatial and temporal profiles, the work presented in this chapter has thoroughly investigated
the effects of filamentation on different materials—the effective parameters so to speak. It was shown that the ablated volume, and therefore also the ablated mass, remained quasi-constant along the propagation length of a filament. This quantity of mass ablated was sufficient for the application of laser filamentation as a sampling tool for plasma based chemical analysis techniques. Ablation quantification was performed within our 12 m laboratory as well as at stand-off distances of 50 m.

By correlation of the known ablation behavior of GaAs, a well characterized semiconductor, with measured relative-fluence profiles of the filament, a clear picture of how the energy reservoir influenced the ablation as well as an ‘effective fluence profile’ were obtained.

The effects of external focusing on filamentation, including: the stability, shape of the fluence profile and peak fluence were investigated. For precision laboratory-based filamentation experiments, the improved pointing stability obtained through external focusing and corresponding change in the fluence profile of the filament that was found to be proportional to the focusing power.

Following filament-induced ablation, post-event sample metrology allowed the characteristic features to be compared with what has been reported for focused fs irradiation. Using semiconductors as a means for comparison, it was found that ablation of material from the sample, laser-induced amorphization of the surface, and re-deposition of matter from the filament-induced plasma re-condensed on the sample surface could all be correlated with what has been observed using focused fs irradiation. The production of sub-micron size particles, both ablated and re-condensed, within the filament-induced plasma (Sec. 6.7) could have implications
for plasma-based spectroscopy as discussed in the context of double-pulse LIBS (Sec. 5.4). The contrast in the ablation observed behavior of titanium and gold samples was attributed to differences in physical and optical material properties. In the case of a carefully engineered gold surface, no sample ablation was observed—a ‘filament mirror’ was created. For titanium, significant the differences in observed ablation behavior were correlated to changes in the nanometer scale surface-feature size and density of the deposited film. Collaborative experiments with ARL allowed for the investigation of multiple-shot filament ablation using a different laser system with longer pulse duration for comparison with the results of previous work conducted at UCF. Both linear and quasi-linear dependences of the ablated mass on the number of pulses were observed for Ti and GaAs, respectively. Despite changes to the sample surface during ablation and the inherent pointing instabilities associated with filamentation, the near linear relationship between number of pulses used for ablation and the quantity of ablated mass could be advantageous for remote material sampling for spectroscopy applications. The plasma that results following filament-induced ablation and the corresponding expansion dynamics are described in the next chapter.
CHAPTER 7. FILAMENT INDUCED PLASMAS

7.1 Introduction

The plasma that follows filament-induced ablation of solids has several unique attributes, for the application to plasma-based spectra-chemical analysis. This work has shown that the expansion of the plasma and the shockwave are correlated to the material specific attributes of filament-induced ablation presented in the previous chapter (CHAPTER 6). A qualitative picture of the energy that was converted into the filament-induced plasma was obtained through the characterization of the shockwave dynamics.

7.2 Dynamics of filament-induced plasmas

Although energy is transferred from the filament to the material on the timescale of the pulse duration, material cannot escape the surface on this ultrafast timescale (Sec. 3.4.2). The dynamics of material ablation, shockwave propagation and plasma formation were characterized by means of ultrafast pump-probe shadowgraph (Sec. 4.4.1), ICCD camera shockwave imaging (Sec. 4.4.2) and time resolve plasma emission spectroscopy (Sec 4.3.1). Following the non-focused filament-induced ablation of titanium (ablation crater shown in Figure 6-6) the resulting air shockwave developed relatively slowly (compared with focused fs ablation), and it propagated away from the sample surface along the axes of the incident filament. After 45 ns, the resulting shock front and contact front (Figure 7-1) had expanded to approximately 150 µm and 100 µm from the sample surface, respectively. The thin layer of shocked air in-between the shock front and contact front was likely to have been weakly ionized; however, a clear ionization front was not observed.
Figure 7-1. Shadowgraph image of the shockwave 45 ns after the non-focused filament-induced ablation of titanium. In the image, the sample is shown on the bottom and the filament was incident from the top. The y-axis depicts the perpendicular expansion of the shock front while the x-axis is the lateral distance along the sample surface.

The lateral shockwave dimension (Figure 7-1) of approximately 480 µm was comparable with the resulting ablation crater diameter (Figure 6-6) of approximately 560 µm (Figure 7-2).

Figure 7-2. Comparison between a) lateral shockwave dimension at 45 ns and b) the resulting crater diameter. Please note that the x-axis has been plotted on the same scale; however, the y-axes are plotted in microns and nanometers for a) and b), respectively.
The different filament-induced ablation behavior of germanium and titanium samples, as was observed by the ‘post mortem’ characterization of the ablation craters (Sec. 6.7), was also clearly observed in the shadowgraph images. For non-focused filament-induced ablation of germanium, the resulting shock front expansion after 45 ns (Figure 7-3) had a lateral expansion that was similar to that of titanium (Figure 7-1); however, the perpendicular expansion was approximately 120 µm as compared with 150 µm for titanium.

![Figure 7-3. Shadowgraph image of the shockwave 45 ns after the non-focused filament-induced ablation of germanium. In the image, the sample is shown on the bottom and the filament was incident from the top. The y-axis depicts the expansion perpendicular to the sample surface the x-axis represents the lateral distance along the sample surface.](image)

In the case of germanium, the contact front was significantly smaller than that observed for titanium. After 45 ns, the lateral and perpendicular extensions of the contact front (Figure 7-3) were approximately 100 µm and 30 µm, measured from the center, respectively. This was consistent with the decreased crater depth and the increased re-deposition of condensed matter within the central crater region that was observed for germanium (Figure 6-22).

The shockwave resulting from non-focused filament-induced ablation of GaAs resulted in shock front expansion after 45 ns (Figure 7-4a) that was similar to what was observed for
titanium (Figure 7-1) and germanium (Figure 7-3) samples; however, the expansion velocity of the contact front was in-between that of titanium and germanium. The increased peak fluence obtained by using a 10 m focal length lens (Figure 6-9), to improve the pointing stability (Figure 6-10) of the filament, resulted in greater expansion velocity of the shock front (Figure 7-4).

Figure 7-4. Shadowgraph image of the shockwave that resulted 45 ns after the a) non-focused and b) focus-assisted filament-induced ablation of GaAs. In the image, the sample is shown on the bottom and the filament was incident from the top. The y-axis depicts the perpendicular expansion of the shock front while the x-axis is the lateral distance along the sample surface.

The shockwave expansion velocity is related to the energy delivered to the plasma, as given by Sedov-Taylor scaling [283, 284]:

\[
R = \lambda \left( \frac{E}{\rho} \right)^{1/(2+\beta)} t^{2/(2+\beta)}
\]

(7-1)

where \( R \) is the radius of the expanding shock front, \( \lambda \) is a constant that is near unity, \( E \) is the energy converted into the plasma, \( \rho \) is the undisturbed mass density of air, \( t \) is the propagation time and \( \beta \) represents the dimensionality of expansion. For planar \( \beta = 1 \), for cylindrical \( \beta = 2 \) and for spherical expansion \( \beta = 3 \). The validity of this expression, however, relies on the assumption of an instantaneous and massless point explosion. For application to laser-generated
shockwave expansion, the pulse duration is assumed to be shorter than \( t \) and the beam radius much smaller than \( R \).

Although the femtosecond duration of the filament was much shorter than the earliest observation time of the shockwave, on the order of a nanosecond, the area of interaction was similar in dimension to that of the shockwave. Therefore, the validity of the Sedov-Taylor relationship during the early stages of filament-induced plasma expansion is questionable. Using focus-assisted filaments for the ablation of GaAs, the expansion was plotted versus time (Figure 7-5) for both lateral and perpendicular directions. An ultrafast pump-probe shadowgraph (Sec. 4.4.1) was used for delay times up to 45 ns and ICCD camera imaging was used for delays longer than 45 ns (Sec. 4.4.2). The shockwave expansion was proportional to \( t^{0.7} \) and \( t^{0.55} \) for perpendicular and lateral dimensions, respectively. From Sedov-Taylor scaling, shockwave expansion proportional to \( t^{2/3} \) is characteristic of 1-dimensional expansion. The lateral extent of the shockwave remained constant until the expansion in the perpendicular dimension had reached approximately an equal value. This occurred after about 200 ns.

![Figure 7-5](image)

*Figure 7-5. Shockwave dynamics following the filament-induced ablation of GaAs at 10 m from the laser using an \( f = 10 \) m focusing lens to increase filament pointing stability.*
From the standpoint of analytical spectroscopy, the validity of spectroscopic plasma temperature calculation as well as other plasma diagnostics relies upon the assumption of local thermodynamic equilibrium (LTE). The 1-dimensional expansion of the filament-induced shockwave was characteristic of a plasma with higher kinetic energy yet lower excitation energy and therefore fewer collisions between atoms and ions. These plasma conditions suggest that, during early times, LTE was not established [284-286].

In contrast to focused laser-induced-plasmas the emission from filament-induced-plasmas was characteristic of a lower electron plasma temperature [116], as seen by a lower degree of ionization among emission species as well as increased molecular emission. Atomic emission decays more rapidly in time (Sec. 3.6) as compared with the molecular emission, and in the case of filament-induced plasmas, the decay of atomic emission occurred in the first couple hundred nanosecond (Figure 7-6). A similar decay profile was observed for focused fs irradiation (Figure 7-7). The molecular emission from organic materials that follows filament-induced plasma formation is often stronger than atomic or ionic emission. For analytical purposes, this molecular emission is not necessarily representative of the sample composition; however, for the characterization of plasma dynamics, it provided a marker for monitoring the dynamics over a longer time period (Figure 7-7). A graphite sample provided both atomic and molecular carbon emission following filament-induced ablation as well as emission from CN radicals. Molecular CN emission from samples not containing nitrogen results from a plasma phase reaction that likely occurs between atmospheric nitrogen and ablated carbon species within the plasma [287-289]. The plasma phase chemistry that leads to molecular formation within filament induced plasma is not yet well understood.
Correlation between atomic carbon and CN molecular emission was found during the initial 100 ns of plasma expansion. Following the decay of atomic carbon emission within the first couple hundred nanoseconds, C$_2$ and CN molecular emission was correlated. After the initial expansion, this longer lived molecular emission, as compared with atomic emission, had a spatial profile that expanded predominately along the sample surface. This preferential lateral extension of the plasma up to 1 µs after the laser pulse was consistent with the type of expansion that was observed using shadowgraph imaging of GaAs (Figure 7-4), Ge (Figure 7-3) and Ti (Figure 7-1). In contrast to this lateral expansion observed using filament irradiation, the shape of the plasma resulting from external focusing of the beam using a 5× microscope objective was spherical (Figure 7-7a).
Figure 7-7. Spectrally resolved plasma emission: from a) focused laser induced carbon plasma and b) filament-induced plasma emission from atomic and molecular species (C, C₂ and CN). The target material was graphite and in the case of filament irradiation, a 5 m focusing optic was used and the resulting profile is shown in c).

External focusing optics were used to help stabilize the filament and the resulting profile was, therefore, characteristic of the 5 m focus that was used (Figure 7-7c). The position of the
filament relative to the resulting plasma image is depicted by the red boxes immediately to the left of the images for 100 ns delay in Figure 7-7b.

The expansion characteristics of filament-induced plasmas—non-spherical in nature—raised the question, ‘is there a preferential emission direction relative to the sample surface?’ For the application of filament-induced plasmas for stand-off spectroscopy, the detection of signal emitted in the backward direction becomes essential.

7.3 Goniometry

The characterization of plasma emission as a function of the detection angle is an area that has received little attention in the literature, despite its importance for stand-off application laser-plasma based sensing techniques. The filament-induced plasma emission from GaAs (Figure 7-8) presented mainly atomic emission lines from gallium (Ga I) in the UV-Visible region of the spectrum. The temporally integrated spectrum was acquired using a Czerny-Turner spectrometer (Sec. 4.3.2) with an ICCD camera to isolate the temporal window of interest and to reduce the short-lived continuum emission. For detection using the spectrometer, the plasma was imaged onto the entrance slit of the spectrometer and therefore the light throughput was proportional to the entrance slit diameter—only a portion of the plasma emission was sampled by the spectrometer. Therefore, to spatially integrate the emission from the entire plasma, the plasma was imaged onto an ICCD camera through a 400 nm band-pass filter to spatially and temporally integrate the emission from a single atomic gallium line at 403.30 nm.
The majority of the ‘useful’ emission, and the best signal-to-noise ratio, was observed between 20 ns and 500 ns after the laser pulse, yet the non-zero spatially-varying background emission was also accounted for by angle tuning the interference filter by 20° to shift the pass-band of the filter off the emission line and capture the background emission. The detection system (Figure 4-6) was rotated around the filament-induced plasma and the single-shot emission was measured versus detection angle between -90° and 90° with respect to the surface normal (Figure 7-9). For each detection angle multiple single shots were acquired and the sample was translated in-between each shot. The error bars in Figure 7-9 represent the standard deviation of 20 single-shot measurements. Because the filament was incident normal to the sample surface, detection at normal incidence was not possible. The detected energy from the filament-induced plasma was strongest for smaller detection angles, relative to the surface normal.
Figure 7-9. Single-shot filament-induced plasma emission from the 403.30 nm gallium line as a function of detection angle, measured with respect to the surface normal. The filament was normally incident on the GaAs surface.

The angular emission dependence, observed from GaAs, likely originated from the profile of ejected material during ablation. The relatively large ablation area, as compared with the ablation depth, that led to the formation of a non-spherical plasma.

The integrated number of counts on the ICCD camera was proportional to the detected energy as well as also directly proportional to the intensity and irradiance at the plane of the detector. This relationship was a result of the detector area and detector solid angle remaining constant. Because the filament-induced plasma emission was dependent on the angle of detection (Figure 7-9), at remote detection distances, the plasma cannot be considered a point source in terms of the intensity pattern being truly isotropic. Even when the plasma is below the resolution limit of the detection optics and therefore spatial variations in the source emission cannot be resolved, the emission is not independent of detection angle—the common assumption for
radiometry of a point source. A more in-depth discussion of the plasma radiometry is given in the following section.

7.4 Radiometry of filament-induced plasmas

Given a type of material and the parameters of an incident laser beam, the ability to predict the emission from a laser induced plasma could have significant implications for laser plasma based spectroscopy, yet to the best of my knowledge, no comprehensive models have enabled this type of emission quantification. The laser ablation uncertainties, represented experimentally by relatively large error bars even in the most careful laboratory experiments, suggest a more empirical approach to the quantification of light emission from filament-induced plasmas. The system used for the characterization of the plasma emission versus detection angle (Sec. 7.3) was calibrated to provide a measure of the spatially and temporally integrated energy emitted by the 403.30 nm gallium emission line. Therefore the number of integrated ICCD counts (Figure 7-9) corresponded to an amount of energy (Joules) seen by the ICCD camera (Figure 7-10).

Figure 7-10. Energy detected as a function of viewing angle for single-shot filament-induced plasma emission from the 403.30 nm gallium line. The detected emission was spatially and temporally averaged. The data is fit reasonably well by a \( \cos^{0.25} \) function.
The finite spatial extend of the plasma, that was detected using an imaging system with an
effective f-number of 4.4, suggests that the plasma should be treated as an extended source rather
than a point source. If the emission from the plasma were assumed to originate from a source
with finite size rather than a point, it would be better described using radiance (L) rather than
intensity (I). The detected flux (\(\phi\)) can be expressed in terms of the source radiance by the
following relationship [290]:

\[
\phi = \int \int \frac{L \partial A_s \cos(\theta_s) \partial A_d \cos(\theta_d)}{r^2} dA_s dA_d
\]

where \(A_s\) and \(A_d\) are the source and detector areas, \(\theta_s\) and \(\theta_d\) denote the angle between the line-
of-sight between the source and detector and vector normal to the surface of the source and
detector, respectively. The line-of-sight distance between source and detector is represented by \(r\).

The angular dependence of the plasma emission was fit to a cosine\(^{1/4}\) functional form (blue line
in Figure 7-10). Using the solid angle of the detection lens (0.041 steradians) and the integration
time of 500 ns, the intensity that corresponded to 1.5 pJ of detected energy was 73.2 µW/ster.

When the source and detector are assumed to be small compared with their separation distance,
the paraxial approximation can be used to simplify Equation 7-2 and express the intensity at the
detector plane in terms of the source radiance:

\[
I = \frac{\partial \phi}{\partial \Omega_d} = \int L \partial A_s \cos(\theta_s) dA_s
\]

where \(\Omega_d\) is the detector solid angle measured in steradians. Using \(L = L_0 \cos(\theta_s)^{3/d}\), the source
exitance \((M)\) can be expressed in terms of radiance using the relationship:
\[ M = \frac{\partial \phi}{\partial A_s} = \int_0^{2\pi} d\varphi \int_0^{\pi/2} [L_0 \cos(\theta_s)^{-3}] \cos(\theta_s) \sin(\theta_s) d\theta_s \]  
(7-4)

\[ M = 2\pi L_0 \int_0^{\pi/2} \cos(\theta_s)^{1/2} \sin(\theta_s) d\theta_s \]  
(7-5)

\[ M = \frac{8}{5} \pi L_0 \]  
(7-6)

Because \( L = L_0 \) at \( \theta_s = 0 \) the flux becomes:

\[ \phi = \frac{8}{5} \pi I = \frac{8}{5} \pi \left( \frac{73.2 \, \mu W}{\text{ster}} \right) = 367.94 \, \mu W \]  
(7-7)

Converting back to energy using the 500 ns integration time window of the ICCD camera, the total radiated energy into half-sphere was 184 pJ. This detected energy at 400 nm corresponded to \( 3.7 \times 10^8 \) photons.

### 7.5 Conclusion

The material specific expansion dynamics of both shockwave and plasma fronts were well correlated with material specific ablation properties. The initial expansion of the filament-induced plasma was slow compared with what has been reported for focused fs irradiation, indicating that less energy was transferred into the plasma. Because the area of interaction associated with filament-induced ablation was relatively large compared with the initial dimension of the shock front, the assumption of a point delivery of the laser energy into the material is questionable. Therefore, a qualitative and not quantitative picture of the energy transferred from filament into the plasma was obtained. The quasi 1-dimensional dynamics of the shockwave, however, could have resulted from the non-spherical geometry of ablation products and casts doubt on the existence of LTE within the early stages of the plasma expansion. The
slowly decaying plasma emission, that resulted from molecular species, provided another means for monitoring the plasma dynamics over a time window of several microseconds. The observed plasma expansion at longer delay times relative to the laser was predominantly along the sample surface. This lateral plasma expansion coupled with the aspect ratio of the plasma, as observed using shadowgraph imaging, suggests that the plasma emission may not be uniform with viewing angle. This angular emission dependence was carefully characterized for single-shot filament-induced plasma using a GaAs sample and the emission intensity was found to be non-uniform with detection angle. Radiometric calculations enabled the retrieval of the total number of emitted photons originating from the transition between two specific atomic energy levels.
CHAPTER 8. CONCLUSION

For the application of femtosecond laser filamentation for laser-ablation-based spectroscopy, the presented work has advanced the current understanding of the interaction of filaments with solid materials as well as the unique attributes of filament-induced plasmas. With numerous demonstrated and potential applications for laser filamentation, the implications of this work extend beyond spectroscopy—any application of femtosecond laser filamentation involving the interaction with a solid target material.

Laser-ablation-based plasma emission spectroscopy techniques, such as LIBS, have primarily been investigated using laser pulses of nanosecond duration. The importance of laser-material interaction on the resulting plasma dynamics was presented in CHAPTER 5, within the framework of our work in the area of longer pulsed lasers applied to double-pulsed LIBS. Although laser-material interaction using ultrashort pulse filamentation constitutes a different regime of interaction, the presented work illustrated the need for fundamental understanding of filament-induced laser ablation (CHAPTER 6) and filament-induced plasma dynamics (CHAPTER 7), for the application of filamentation to spectroscopy.

Through quantification of the filament-induced mass ablation, it was shown that single-shot ablation of GaAs produced sufficient ablated mass for the application of laser filamentation as a sampling tool for plasma based spectroscopy techniques such as LIBS. Furthermore, the ablated mass was shown to remain quasi-constant with propagation distance over the length of our 50 m indoor laser range. The influence of the filaments’ energy reservoir on the ablation behavior of GaAs was characterized using a measured relative fluence profile along with the
published values for the focused femtosecond laser induced breakdown threshold. This relative fluence measurement also allowed an ‘effective fluence profile’ to be determined. The effects of external focusing on the measured filament fluence profile as well as the material ablation behavior were quantified. Although the use of an external focusing optic accelerates the onset of filamentation and, as shown, improves the pointing stability, the fluence profile is also affected. The use of external focusing for laboratory-based filamentation experiments has become common practice in the community; however, this work clearly illustrates the differences of single-shot and single-filament ablation focused-assisted and non-focused filamentation conditions. This difference becomes important when discussing filamentation effects for propagation distances longer than only a few meters.

Beyond the quantification of filament-induced mass removal, sample metrology allowed for characterization of sub-micron size surface features and particles. The production of sub-micron particles likely resulted from re-condensation of ablated mass within the filament-induced plasma (Sec. 6.7) followed by re-deposition on the sample surface. The presence of these nanoparticles within the plasma could have implications for plasma-based spectroscopy, as discussed in the context of double-pulse LIBS (Sec. 5.4).

Physical and optical material properties were observed to have significant effects on the filament-induced ablation behavior. The most pronounced effect was the complete lack of ablation observed on a gold sample. Using two titanium samples with similar compositions yet different physical properties, differences were observed in the ablation depth as well as the size and density of nanoparticle on the surface.
Through collaborative experiments with ARL, comparison of the work conducted at UCF as well as the investigation of multiple-shot filament ablation was performed using a laser system with longer pulse duration—100 fs rather than 50 fs. The dependence of ablated mass on the number of pulses was observed to have a linear and a quasi-linear dependence on the number of pulses for Ti and GaAs samples, respectively. The multi-shot ablation of titanium resulted in the formation of clear periodic surface structures after only 10 shots. Considering the physical and optical changes to the sample surface, these laser-induced surface features have many potential applications. For spectroscopy applications, however, the near linear dependence of the mass ablation with number of pulses is counterintuitive considering the surface restructuring, yet the constant mass ablation per shot is advantageous.

The relatively slow initial expansion of the plasma and corresponding air shockwave, relative to the focused case, suggests that a limited amount of energy was transferred to the plasma during filament-induced ablation. The relatively large interaction area associated with filament-induced ablation, however, excluded the Sedov-Taylor model of a blast wave originating from a point. The quasi-linear expansion of the shockwave in both perpendicular and lateral directions (relative to the surface) was consistent with the observed expansion of molecular plasma species. The non-spherical expansion of ablation products at early times and quasi-linear shockwave expansion suggests that LTE may not have occurred during the early stages of the plasma expansion, as a result of a reduced number of collisions between atoms and ions in the plasma.
The preferential plasma expansion along the sample surface, coupled with the aspect ratio of the plasma observed using shadowgraph imaging, suggests that the plasma emission may not be uniform as a function of detection angle. Characterization of the angular emission dependence from a GaAs sample was performed for single-shot filament-induced plasmas and preferential emission intensity normal to the sample surface was observed. From goniometric measurements of the plasma, the number of emitted photons originating from the transition between two specific atomic energy levels was obtained through radiometric calculations.

In summary, the work presented in this dissertation has advanced the current understanding of single-shot/single-filament effects on the ablation of solid materials as well as the understanding of filament-induced plasma dynamics. This work has laid the foundation for further quantitative studies of multiple filamentation.

8.1 Outlook and future work

A logical progression of the filamentation work presented here, within the framework of single filamentation, would be the extension to multiple filamentation. Some of the potential limitations of single filamentation for spectroscopy applications could potentially be improved by using multiple filamentation. Multiple collinear filaments offset temporally could potentially increase the plasma temperature, advantageous for increasing the strength of the plasma emission, the degree of ionization among plasma species and to potentially improve thermodynamic equilibrium conditions. The spatial control of multiple filaments, potentially with overlapping energy reservoirs, could possibly allow the plasma dimensions to be tailored such that the emission is enhanced in a certain direction.
REFERENCES


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