Growth and Characterization of Thermoelectric Ba₈Ga₁₆Ge₃₀ Type-I Clathrate Thin-Films Deposited by Pulsed Dual-Laser Ablation

by

Robert H. Hyde

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
Department of Physics
College of Arts and Sciences
University of South Florida

Co-Major Professor: Pritish Mukherjee, Ph.D.
Co-Major Professor: Sarath Witanachchi, Ph.D.
  Xiaomei Jiang, Ph.D.
  Dale Johnson, Ph.D.
  George S. Nolas, Ph.D.

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DEDICATION

I dedicate this work to my parents, Mrs. Kay A. Hyde and the late Mr. Harry W. Hyde, who inspired and encouraged the completion of this doctoral degree.
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LIST OF ABBREVIATIONS

Å angstrom
ArF argon fluorine
Ba₈Ga₁₆Ge₃₀ Barium Gallium Germanium
C heat capacity
CA clear aperture
CCD charge coupled device
CJC cold-junction compensation
CO₂ carbon dioxide
CWL center wavelength
DC direct current
ΔT change in temperature
ΔV change in voltage
e electron charge
E_F Fermi energy
f Ladenurg’s oscillator strength
ν₁ laser frequency
νₚ plasma resonant frequency
g upper level statistical weight
Hz hertz
IR infrared
<table>
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<tr>
<th>Abbreviation</th>
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<tr>
<td>ICCD</td>
<td>intensified charge coupled device</td>
</tr>
<tr>
<td>I</td>
<td>current</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>KrF</td>
<td>krypton fluorine</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
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<tr>
<td>$\kappa$</td>
<td>thermal conductivity</td>
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<tr>
<td>$\lambda$</td>
<td>wavelength</td>
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<tr>
<td>MOCVD</td>
<td>metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>micrometer</td>
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<tr>
<td>$\mu$V</td>
<td>microvolt</td>
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<td>ns</td>
<td>nanosecond</td>
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<tr>
<td>OES</td>
<td>Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>OMA</td>
<td>optical multi-channel analyzer</td>
</tr>
<tr>
<td>$n(E)$</td>
<td>density of states</td>
</tr>
<tr>
<td>PGEC</td>
<td>phonon glass electron crystal</td>
</tr>
<tr>
<td>$\alpha^2\sigma$</td>
<td>Power Factor</td>
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<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>$q$</td>
<td>carrier charge</td>
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<tr>
<td>Symbol</td>
<td>Description</td>
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<td>TEA</td>
<td>transversely-excited atmospheric-pressure</td>
</tr>
<tr>
<td>UV</td>
<td>ultra-violet</td>
</tr>
<tr>
<td>$V$</td>
<td>voltage</td>
</tr>
<tr>
<td>$V_H$</td>
<td>high voltage</td>
</tr>
<tr>
<td>$V_L$</td>
<td>low voltage</td>
</tr>
<tr>
<td>XeCl</td>
<td>xenon chloride</td>
</tr>
<tr>
<td>YSZ</td>
<td>yttrium stabilized zirconium</td>
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<tr>
<td>$ZT$</td>
<td>figure-of-merit</td>
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ABSTRACT

The on-going interest in thermoelectric (TE) materials, in the form of bulk and films, motivates investigation of materials that exhibit low thermal conductivity and good electrical conductivity. Such materials are phonon-glass electron-crystals (PGEC), and the multi-component type-I clathrate $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ is in this category. This work reports the first investigation of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ films grown by pulsed laser deposition (PLD).

This dissertation details the in-situ growth of polycrystalline type-I clathrate $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ thin-films by pulsed laser ablation. Films deposited using conventional laser ablation produced films that contained a high density of particulates and exhibited weak crystallinity. In order to produce high quality, polycrystalline, particulate-free films, a dual-laser ablation process was used that combines the pulses of (UV) KrF excimer and (IR) CO$_2$ lasers that are temporally synchronized and spatially overlapped on the target surface. The effect of the laser energy on stoichiometric removal of material and morphology of the target has been investigated. In addition, in-situ time-gated emission spectroscopy and imaging techniques were used to monitor expansion of components in the ablated plumes. Through these investigations, the growth parameters were optimized not only to significantly reduce the particulate density but also to produce large area stoichiometric films. Structure and electrical transport properties of the resultant films were also evaluated. This work provides new insight toward the in-situ growth of complex multi-component structures in thin-film form for potential TE applications.
CHAPTER 1:
INTRODUCTION

The increasing need for energy production and conservation has motivated interest in technologies that address energy harvesting [1]. Waste-heat recovery through the application of thermoelectric materials (TE) can play a major role in this area [2-5]. The impact that TE materials will have on the energy crisis is a matter of debate [6], however, niche military, space [7], and commercial products have shown promise over the past decade. Small scale thermo-generators for low power consumption in high-volume commercial applications are the most promising [8]. Vehicle exhaust heat recovery has considerable potential benefit and along with a U.S. Department of Energy (DOE) goal of ~10% improved fuel economy is stimulating on-going research [7-9]. TE materials have found applications as self-powered monitors, transponders, and temperature warning systems [9]. Other viable applications include localized active cooling or heating of devices such as micro-processors, laser diodes, detectors, and biological specimens [10-12]. However, the main shortcoming with current thermoelectric materials is their poor efficiency [3]. From the experimental point of view, one of the motivations is to have the ability to grow TE materials in thin-film form for devices with improved efficiencies.
This chapter describes the physical properties that contribute to the TE conversion efficiency, and material systems and structures used in TE devices. Commonly used film fabrication techniques will be discussed, as well as the PLD that was utilized.

1.1. Thermoelectrics

A basic review of thermoelectrics (TE) is presented as well as the current focus for improving TE materials being researched. The novel materials known as clathrates will be discussed, and thin-film TE structures and their deposition techniques will be reviewed.

1.1.1. Basic Review

In a conductor or semiconductor the free carriers (electrons and holes) carry both charge and heat and can be induced to diffuse through the material (Figure 1.1) [13, 14]. The diffusing carriers are scattered by impurities, imperfections, and lattice vibrations (phonons) and these hot and cold carriers diffuse at different rates. The Fermi-Dirac distribution for a hot and cold temperature is depicted in Figure 1.1 [15, 16]. Within the

Figure 1.1. The Seebeck effect for an isolated conductor in a uniform temperature gradient ($\Delta T$). The Fermi-Dirac diagrams indicate the energy states for a hot and a cold temperature. The higher energy carriers diffuse from the hot side to the cold side generating a voltage potential ($\Delta V$).
temperature gradient ($\Delta T$) the average energy per electron in an isolated conductor is greater in the hot end. Consequently, the more energetic electrons diffuse toward the cold region until a potential difference ($\Delta V$) is built up which prevents further diffusion.

The basis of this process is called the Seebeck or thermoelectric effect, discovered in 1821. Thomas Seebeck observed when two dissimilar conductors, $a$ and $b$, are joined (Figure 1.2) and the junctions are held at two different temperatures, $T_1 > T_2$, a voltage difference ($\Delta V$) develops that is proportional to the temperature difference ($\Delta T$). The $\Delta V$ and $\Delta T$ are related by an intrinsic property of the materials called the Seebeck coefficient or thermopower ($\alpha$) where $\alpha_{ab}$ is defined as the differential Seebeck coefficient between materials $a$ and $b$ such that:

$$\alpha_{ab} = \frac{\Delta V}{\Delta T}$$  

(1.1)

for small $\Delta T$ as $T \rightarrow 0$.

![Figure 1.2. Schematic diagram of the open circuit Seebeck effect for two dissimilar conductors $a$ and $b$ with junctions at positions 1 and 2, held at temperatures $T_1 > T_2$, respectively.](image)

A reversal of this process is known as the Peltier effect, discovered in 1834. It was observed when an electric current flows through the junction of two dissimilar metals, heat is exchanged [17, 14]. If a current source is applied across the points 3 and 4 (Figure 1.2), then heat is either absorbed or rejected depending on the direction of the
current. The Seebeck coefficient ($\alpha$) and the Peltier effect are related to each other in the definition of the Peltier coefficient ($\Pi$) where:

$$\Pi = \alpha_{ab} T$$  \hspace{1cm} (1.2)

where $T$ is the temperature of the junction. The rate of heating ($Q$) or cooling is given by:

$$Q = \alpha_{ab} IT$$ \hspace{1cm} (1.3)

where $I$ is the current through the junction.

The Seebeck effect and Peltier effect are the foundation for solid state $TE$ devices that can be used to directly convert heat into electricity for power generation, or for refrigeration, depending the configuration (Figure 1.3) [2, 3]. A $TE$ couple, is made up of two types of semiconductor materials, an $n$-type (electron majority carriers) and a $p$-type (hole majority carriers). The two branches of the device are connected by a metallic contact to form an electrical series, but thermally parallel circuit [13, 14]. The Seebeck effect is temperature-gradient driven; a heat source applied to one side will drive the

![Figure 1.3. Arrangement of thermoelectric modules for (a) power generation by the Seebeck effect and (b) refrigeration by the Peltier effect.](image-url)
majority carriers toward the cooler region (Figure 1.3a). This type of TE configuration will produce a voltage that can be utilized drive a current through a load resistance ($R_L$) for power-generation.

The Peltier effect is current driven; an electric current applied to the material system diffuses the hot carriers through the circuit (Figure 1.3b). The electrons in $n$-type material will flow against the direction of the current and holes in $p$-type material will flow with the current direction. Since ideal ohmic metal/semiconductor contacts at thermal equilibrium share Fermi levels ($E_f$), heat will be absorbed or emitted as carriers (electrons and holes) cross the junctions [18, 19]. For example, as current passes through the metal/$n$-type semiconductor junction an electron acquires energy (cooling) as it enters the conduction band. Energy is released (heating) as an electron passes through an $n$-type semiconductor/metal junction (Figure 1.4). Thus, this TE configuration provides

**Figure 1.4.** The energy band diagrams for ideal ohmic metal-semiconductor junctions at thermal equilibrium for a TE refrigeration device. The thermal energy absorption and emission as the carriers (electrons and holes) cross the junctions between the semiconductor material and metal contacts.
refrigeration capability with no moving parts.

A \( TE \) couple is consists of \( TE \) material segments \( a \) and \( b \), which are \( p \)-type and \( n \)-type, respectively. The efficiency (\( \eta \)) of a \( TE \) power generation couple is measured as the ratio of electrical power (\( P_L \)) delivered through the load resistance (\( R_L \)), relative to the heat flow (\( Q_H \)) into the hot side of the \( TE \) couple. The electrical power is given by \( P_L = I^2 R_L \) where \( I \) is the current through \( R_L \).

\[
\eta = \frac{P_L}{Q_H}
\]  

(1.4)

The \( Q_H \) input is comprised of three terms. The heat flow through the \( TE \) couple due to the thermal conductance (\( K\Delta T \)); the heat absorbed at the hot junction due to the Peltier coefficient (\( Q = \alpha_{ab} I T_H \)), equation (1.3); and the heat due to Joule heating (\( \frac{1}{2}I^2 R \)) of the \( TE \) couple with the assumption that it is divided between the hot and cold sides. \( K \) is the total thermal conductance of materials \( a \) and \( b \) in parallel, and \( R \) is the series resistance of \( a \) and \( b \). Therefore, \( Q_H \) is given by:

\[
Q_H = K\Delta T + \alpha_{ab} I T_H - \frac{1}{2} I^2 R
\]  

(1.5)

then the power generation efficiency (\( \eta \)) is given by:

\[
\eta = \frac{IR_L}{K\Delta T + \alpha_{ab} I T_H - \frac{1}{2} I^2 R}
\]  

(1.6)

where \( \Delta T = T_H - T_C \), and \( \alpha_{ab} = \alpha_p - \alpha_n \) where \( \alpha_p \) and \( \alpha_n \) are the Seebeck coefficients of the \( p \)-type and \( n \)-type materials, respectively.

The efficiency (\( \varphi \)) of \( TE \) refrigeration is measured by the coefficient of performance (COP), defined as the ratio of the heat absorbed (\( Q_C \)) to the electrical power input. The rate of the heat absorbed is given by:
The power input \( P \) is given by:

\[
P = \alpha_{ab} I \Delta T + I^2 R
\]  

(1.8)

where the applied voltage to the TE couple is balanced between the resistance \( R \) of the TE segments and the Seebeck voltage due to the \( \Delta T \) between the junctions. The efficiency \( (\phi_C) \) of refrigeration is then given by:

\[
\phi_C = \frac{Q_C}{P} = \frac{(\alpha_p - \alpha_n)T_c I - \frac{1}{2} I^2 R - K\Delta T}{(\alpha_p - \alpha_n)I \Delta T + I^2 R}
\]  

(1.9)

The efficiency \( (\phi_H) \) of the heat released by the hot side for TE heating is obtained by substitution of \( T_H \) for \( T_C \) in equation (1.9).

The performance of a TE couple can be evaluated at a specified temperature by the figure-of-merit \( (Z) \) where:

\[
Z = \frac{\alpha_{ab}^2}{RK}
\]  

(1.10)

If the geometries of the segments \( a \) and \( b \) are matched to minimize heat absorption, then the segment cross-sectional area \( (A) \) and length \( (L) \), can optimize the \( Z \) of a TE couple. An optimization of \( Z \) occurs if the product \( RK \) is minimized, such that when:

\[
\frac{L_n A_p}{L_p A_n} = \left( \frac{\rho_p \kappa_n}{\rho_n \kappa_p} \right)^{\frac{1}{2}}
\]  

(1.11)

The figure-of-merit for the couple can then be rewritten in terms of the two materials, an \( n \)-type and a \( p \)-type, where:
\[ Z = \frac{(\alpha_p - \alpha_n)^2}{\left( \rho_p \kappa_p \right)^{1/2} + \left( \rho_n \kappa_n \right)^{1/2}} \]  

(1.12)

or as the dimensionless figure-of-merit (ZT):

\[ ZT = \frac{(\alpha_p - \alpha_n)^2 T}{\left( \frac{\kappa_p}{\sigma_p} \right)^{1/2} + \left( \frac{\kappa_n}{\sigma_n} \right)^{1/2}} \]  

(1.13)

The performance of an individual TE material segment relies directly on the ZT [14]. The parameter ZT is then given by:

\[ ZT = \frac{\alpha^2 \sigma T}{\kappa} \]  

(1.14)

where \( \alpha \) is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, \( T \) is the temperature of interest, and \( \kappa \) is the total thermal conductivity. The \( \kappa \) is approximately described as:

\[ \kappa = \kappa_L + \kappa_e \]  

(1.15)

where \( \kappa_L \) is the lattice thermal conductivity and is the heat conducted by phonons (lattice vibrations). The electronic thermal conductivity \( (\kappa_e) \) is the heat conducted by mobile electrons. Since the \( \kappa_e \) for TE materials is proportional to \( \sigma \) via the Wiedemann-Franz law [5] given by:

\[ \kappa_e = \sigma LT \]  

(1.16)

where \( L \) is the Lorentz number \((2.45 \times 10^{-8} \text{ V}^2\text{K}^{-2} \) for free electrons). The product \( \alpha^2 \sigma \) is referred to as the electrical power factor and is a value commonly reported as an indicator of TE performance.

The early application of the TE effect was metal thermocouples which are still widely used today. During the 1950s and 1960s extensive research was conducted on
materials such as alloys of Bi$_2$Te$_3$ and Si$_{1-x}$Ge$_x$ for thermoelectric applications. These materials remain state-of-the-art for their specific temperature use. In the 1990s, resurgence in the field began with advances in novel processes for producing bulk materials and progress in thin-film growth techniques [11].

1.1.2. Current Thermoelectric Materials Research

At room temperature, $T = 300$ K, desired values for the thermoelectric parameters are $\alpha = 225$ $\mu$V/K [20], $\sigma = 10^5$ $\Omega^{-1}$m$^{-1}$, and $\kappa = 1.5$ W/m·K, which results in a $ZT \approx 1$. These values are typical for the best TE materials such as Bi$_2$Te$_3$ and Sb$_2$Te$_3$ alloys, which are presently used by industry in devices that operate near room temperature and are well investigated [2, 21]. Current TE devices operate at an efficiency of about 5-6%. By increasing $ZT$ by a factor of 4 predicted efficiencies can increase to 30% [3].

A comparison of various $n$-type and $p$-type TE materials is shown in Figure 1.5 where the $ZT$ peaks for each material such that each material has an optimal operating temperature range [5]. CsBi$_4$Te$_6$ ($p$-type) has shown promise for low temperature applications (100 - 200 K) [22, 23]. Mid-temperature range (500-900 K) power generation materials have been based on tellurides like LAST (Lead-Antimony-Silver-Telluride, $n$-type) and TAGS (Te-Ag-Ge-Sb, $p$-type) such as (AgSbTe$_2$)$_{0.15}$(GeTe)$_{0.85}$. TAGS has been shown to be more efficient than PbTe but is very expensive. High temperature TE generators (>900K) have used Si-Ge alloys ($n$-type and $p$-types) as well as La$_2$Te$_3$ ($n$-type) and Yb$_{14}$MnSb$_{11}$ ($p$-type). Lower thermal conductivity has been achieved with materials such as $\beta$-Zn$_4$Sb$_3$ (0.9 W/m·K) [24], $n$-type PbTe (0.15 W/m·K) [24], and inhomogeneous nano-structured materials such as SALT (Sodium-Antimony-
Lead-Telluride) and LASTT (Lead-Antimony-Sodium-Tin-Telluride) \cite{3, 5}.

Current research is aimed at increasing the \( \text{ZT} \) by maximizing the power factor \( (\alpha^2\sigma) \) and/or minimizing the thermal conductivity \( (\kappa) \), or finding materials capable of operating in new or broader temperature ranges \cite{20}. A maximized power factor implies that a high voltage and current are generated, and a low \( \kappa \) allows a larger \( \Delta T \) to be created across the material \cite{2-5}.

Increasing the power factor \( (\alpha^2\sigma) \) involves increasing \( \alpha \) and \( \sigma \) together. In reality, it is difficult to enhance \( \alpha \) without lowering \( \sigma \). Since \( \alpha \) is the energy transported per carrier

\[
\alpha \approx \frac{C}{q} \tag{1.17}
\]

where \( C \) is the specific heat and \( q \) is the charge of the carrier, a low \( \sigma \) gives rise to high \( \alpha \).
The $\alpha$ and $\sigma$ can be adjusted through doping that changes the free carrier concentration. Since these two parameters typically change in opposite directions, a compromised set of values needs to be achieved such that there is a peak power factor through optimization of the carrier concentration ($n$) [5]. Depending on the material system, the optimum carrier concentration typically occurs at $10^{19}$ to $10^{21}$ cm$^{-3}$, a concentration found in heavily-doped semiconductors (Figure 1.6). To effectively minimize minority carrier contributions, leading high-mobility carriers, the direct band-gap needs to be large enough, on the order of $\approx 10 k_B T$, where $k_B$ is the Boltzmann constant ($1.381 \times 10^{-23}$ J/K) [25]. For semiconductors, the carriers must be thermally excited across the band-gap for conduction to occur, and the temperature-dependence of the electrical conductivity is approximated by:

$$\sigma \approx \sigma_0 e^{\frac{E_g}{k_B T}}$$  \quad (1.18)

*Figure 1.6.* A comparison of the Seebeck coefficient ($\alpha$), power factor ($\alpha^2 \sigma$), and conductivity ($\sigma$) as a function of the carrier concentration ($10^x$) [5].
There are two primary ways to achieve a high conductivity, by having a very small band-gap to excite across \((E_g \approx 10k_bT, 0.25 \text{ eV at 300 K})\), or by having very high-mobility carriers \((\mu \approx 2000 \text{ cm}^2/\text{V}\cdot\text{s})\) [20]. Optimizing the power factor of a material or system would have to be based on band-gap size, shape and width of the bands near the Fermi level \((E_F)\), and the carrier effective masses and mobilities [25].

A common characteristic of recently developed thermoelectrics with \(ZT > 1\) is that most have lattice thermal conductivities \((\kappa_L)\) that are lower than the current commercial materials. The lattice thermal conductivity \((\kappa_L)\) component of the total thermal conductivity is the only parameter not determined by the electronic structure [2, 3]. Lowering \(\kappa_L\) would come at the cost of lowering \(\sigma\) which is not desirable in a \(TE\) material. A reduced lattice thermal conductivity directly improves the \(TE\) efficiency, and allows re-optimization of the carrier concentration for additional \(ZT\) improvement.

Productive strategies to improve the \(ZT\) related to minimizing the thermal conductivity are the use of materials with intrinsically low \(\kappa_L\), and to scatter phonons within the unit cell or structure. Materials with intrinsically low \(\kappa_L\) follow the phonon-glass electron-crystal (PGEC) approach. The PGEC approach is a concept introduced by Slack (1995) as a guide for new \(TE\) materials with improved properties [26]. An ideal PGEC material would have the thermal conductivity associated with amorphous materials (“phonon-glass”), and the electronic properties associated with good semiconductor single crystals (“electron-crystal”). Scattering phonons can be accomplished by (i) creating rattling structures or point defects such as interstitials, vacancies or by alloying, (ii) the use of complex crystal structures, (iii) increasing the lattice period, and (iv) by scattering phonons at interfaces utilizing boundary scattering.
1.1.3. Clathrates

PGEC materials that can satisfy these strategies include the class of novel materials known as clathrates [27, 28]. Inorganic clathrates were first systematically investigated in the 1960s with Na$_8$Si$_{46}$ (Kasper et al., 1965), Si and Ge (Cros et al., 1968), and Sn clathrates (Gallmeier et al., 1969) [29]. Type-I inorganic clathrates are characterized by a framework of ‘host’ atoms which occupy sites at the vertices of face-sharing polyhedral ‘cages’ which enclose loosely bond ‘guest’ atoms. A general chemical formula for type-I clathrates can be written as A$_8$B$_y$Y$_{46-y}$, where A represents the guest atom (Group IIA, alkaline-earth metal, Sr, Ba, or Eu), and B framework substituting atom (Group IIIB, Ga or In), and Y (Group IVB, Si, Ge, or Sn) represent the framework atoms. The host atom cages form two pentagonal dodecahedrons and six tetrakaidecahedrons (hexagonal truncated trapezohedron) per cubic unit cell [29, 30]. The 12 sided (12 pentagons), 20 atom dodecahedron and the 14 sided (12 pentagons and 2 hexagons), 24 atom tetrakaidecahedron cages with the enclosed guest atom are shown in Figure 1.7a. The unit cell crystal structure highlighting the dodecahedra outlined at the center of Figure 1.7b, and the tetrakaidecahedron is outlined at the right of the figure. The green shaded spheres represent atoms forming the host framework, and the guest atoms inside the polyhedra are represented in shades of blue. Type-I clathrate belongs to the crystallographic cubic space group Pm-3n, and in the Wyckoff position notation the host atoms are found at three different sites, 6c, 16i, and 24k (see Appendix A) and the centers of the cages are denoted 2a and 6d for the dodecahedron and tetrakaidecahedron cages, respectively.
The fully occupied \((A_xB_yY_{46-y})\) host-atom framework of the type-I clathrate contains 46 tetrahedrally coordinated host atoms in the unit cell. The geometrical arrangement of the 46 host atoms leaves 8 voids per unit cell for the guest atoms to occupy. An illustrative description of the three dimensional structure is shown in Figure 1.8a-d, where depth perspective has been added for clarity. The one guest atom is located at each corner \((2a)\) and two on each face \((6d)\) of the cubic unit cell (Figure 1.8a). Part of the structure can be envisioned where a dodecahedron cage encloses the guest atom at each \(2a\) site (Figure 1.8b). Each tetrakaidecahedron cage encloses a \(6d\) site guest atom where these cages are joined by their hexagonal faces (Figure 1.8c). The complete structure with the unit cell outlined is illustrated in Figure 1.8d, which can be visualized as the dodecahedron cages joined through the \(16i\) sites with vacancies at the \(6c\) sites. The dodecahedron cage is a subunit present in all inorganic clathrates and filling the \(6c\) sites form the outline of the tetrakaidecahedron cages. Describing the type-I clathrate with this

**Figure 1.7.** The type-I clathrate composed of the (a) face-sharing pentagonal dodecahedron and tetrakaidecahedron, and the (b) cubic unit cell with the polyhedra outlined in red. The Wyckoff positions of the guest and framework atoms are indicated.
manner has been used to help explain the preference for vacancies and lower valence host elements on the 6c site [124].

The loosely bound guests, or ‘rattlers’, in these crystalline materials can undergo

Figure 1.8. Components of the type-I clathrate structure with (a) eight guest atoms on the corners, one on center, and twelve on the faces of the cubic unit cell, and the (b) nine dodecahedron cages, (c) the twelve tetrakaidecahedron cages, and (d) the complete host-guest schematic.
large, localized low-frequency vibrations, which in turn can scatter the heat-carrying acoustic phonons resulting in thermal conductivities with magnitudes similar to amorphous materials. The guest-host interaction in clathrates continues to be of scientific interest. It has also been demonstrated that the transport properties can be optimized through Si substitution within the Ga-Ge framework [31-33] and manipulation of the carrier concentration [34].

The type-I class of clathrates meet desired features for possible $ZT$ improvement with their intrinsically low $\kappa$, complex crystal structure with the phonon scattering rattler. As a result of the interesting properties and technological promise of type-I clathrates, the bulk properties of these materials have been studied extensively using a wide range of experimental and theoretical techniques [34].

1.1.4. Thin-Film Thermoelectric Structures

Phonon scattering at interfaces leads to the use of multiphase composites mixed on the nanometer scale. These nanostructured materials can be formed as thin-film hetero-structures and superlattices, or as intimately mixed composite structures. $TE$ materials in thin-film form offer promise for $ZT$ enhancement [35]. Three thin-film approaches have been suggested. The first approach uses quantum-confinement effects to obtain an enhanced density of states near the Fermi level. The second approach employs phonon-blocking/electron-transmitting superlattices. These structures utilize the acoustic mismatch between the superlattice components to reduce $\kappa_L$, rather than using the conventional alloying approach, thereby potentially eliminating alloy scattering of carriers. The third thin-film approach is based on thermionic effects in heterostructures
Thin-film heterostructures, or superlattices, consist of alternating thin layers (2-10 nm each) of different materials stacked periodically (~100 µm total thickness). The lattice mismatch and electronic potential differences at the interfaces, and resulting phonon and electron interface scattering and band structure modifications can be exploited to reduce phonon heat conduction, i.e. $\kappa_L$, while maintaining or enhancing the electron transport. This in turn, improves the thermoelectric figure of merit [35].

1.1.5. Thin-Film Deposition Techniques

Films of $TE$ materials have been deposited by a variety of fabrication techniques. Research-based thin-film deposition techniques include molecular beam epitaxy (MBE) [37] and low-pressure chemical vapor deposition (CVD) [38] of Si-Ge alloys; low temperature metal organic chemical vapor deposition (MOCVD) [39, 40], flash evaporation [41, 42], MBE [43], sputtering [44], and pulsed laser ablation (PLA) [45] of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ alloys.

The method of PLA profitably differs from the thermal methods of continuous deposition of thin semiconductor films. The presence of a large fraction of excited atoms and ions allows lower growth temperatures, and a high nucleation rate allows the deposition of thin continuous films, on the order of several nanometers. In addition, since an insignificant mass of the target material evaporates for one pulse, the film thickness can be precisely controlled by the number of laser pulses. In some cases, the quality of the films obtained by laser ablation is comparable with the quality of films grown by MBE [46]. One of the main advantages of laser ablation for film growth is the ability of this process to closely reproduce the target stoichiometry in the deposited film [47-49].
For a target that contains elements with a wide variation of physical properties, pulsed laser ablation is uniquely suited for the growth of complex structured, multi-component films from a single composite target such as Ba$_8$Ga$_{16}$Ge$_{30}$.

1.2. Pulsed Laser Vaporization and Deposition

Pulsed laser deposition (PLD) is often described as a three-step process consisting of (i) vaporization of a target material, (ii) transport of the vapor plume, and (iii) film growth on a substrate (Figure 1.9) [50, 51]. During the first step, a pulsed laser beam strikes the surface of the source material, a rotating target, and the energy from the laser rapidly evaporates the target’s surface. In most materials, the radiation is absorbed by only the outermost layers of the target, to a depth on the order of fractions of a micrometer. The short laser pulses, lasting less than 50 ns, cause the temperature of the surface to rise rapidly to thousands of degrees Celsius, but the temperature of the target

![Figure 1.9. Diagram of the pulsed laser deposition process depicting the pulsed beam (i) vaporization of the target surface, (ii) transport of the vapor plume, and (iii) growth of the film on the substrate.](image-url)
bulk remains unchanged. The rapid, non-equilibrium heating produces evaporants along with the characteristic luminous plasma that expand and propagate, as the second step. This vaporized material then deposits on the substrate, the third step, producing a film with composition typically identical to that of the target surface. The ability to reproduce the composition of the target in the film may be the highest benefit of PLD [52].

This technique has many unique advantages for thin-film deposition (Table 1.1). An energy source (laser) outside of the deposition chamber produces a highly forward-directed and confined plume of materials, which can be deposited with less contamination than the unconfined plasma in a sputter process. In complex multicomponent material deposition with conventional evaporation methods, the various cations come from different sources. To produce the right mixture in the deposited film, the rate of arrival of each species must be monitored and controlled. PLD does not require such monitoring, because the composition of the film typically replicates the composition of the target, referred to as congruent evaporation and stoichiometric deposition. Producing multilayer materials can also be accomplished rather easily with PLD, because different targets can be alternately positioned in the path of the laser beam which is done with a controlled target carousel. PLD is a good technique for depositing

<table>
<thead>
<tr>
<th>Property</th>
<th>Effect on film properties</th>
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<tr>
<td>Congruent evaporation</td>
<td>Stoichiometry</td>
</tr>
<tr>
<td>High kinetic energy of species</td>
<td>Crystalline structure. Sputtering of light atoms</td>
</tr>
<tr>
<td>High instantaneous evaporation rates</td>
<td>Low background gas incorporation. Crystalline structure</td>
</tr>
<tr>
<td>Low power input</td>
<td>Low thermal radiation</td>
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<td>Local evaporation</td>
<td>Preservation of source purity</td>
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<tr>
<td>Particulate ejection</td>
<td>Degradation of optical, electrical properties</td>
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</table>
extremely pure films. In most processes the film includes contaminants. For example, in thermal and electron-beam evaporation a container is used to hold the source material, and the high temperatures needed to evaporate the source materials can also evaporate parts of the container thereby contaminating the deposition process. In metal organic chemical vapor deposition (MOCVD), volatile organic molecules transport the desired cations from the source to the film, and fragments of the organics can end up in the film [52].

It is desirable to have the photon energy of the laser greater than the band gap of the material which is being ablated, thus giving lower densities required for ablation. The photon energy, \( E_{\lambda} \), is given by;

\[
E_{\lambda} = \frac{hc}{\lambda}
\]

where \( h \) is Plank’s constant \((6.626 \times 10^{-34} \text{ J\cdot s})\), \( c \) is the speed of light \((2.998 \times 10^8 \text{ m/s})\), and \( \lambda \) is the laser wavelength.

The laser power density at the target surface can be divided as low \((< 10^6 \text{ W/cm}^2)\), intermediate \((> 10^6 \text{ W/cm}^2 \text{ and } < 10^8 \text{ W/cm}^2)\), and high \((>10^8 \text{ W/cm}^2)\). The intermediate to high power density regimes correspond to typical PLD laser fluences of 1 to 6 J/cm\(^2\) with laser pulse widths of 20 to 60 ns. An advantage of laser evaporation is the small heat content of the evaporation target due to the small size of the evaporating volume and shorter radiation time of the pulsed laser. The small volume of heated material is defined by the area of the laser spot size at the target surface and its absorption heated depth \((d_H)\). This volume is quickly brought to boiling temperature which then rapidly cools, by conduction into the bulk of the target, upon termination of the laser pulse. These cycle times are on the order of milliseconds and are conducive for congruent evaporation [53].
This process is depicted in Figures 1.10 and 1.11. The dominant mechanisms involved in this process are found to depend on laser parameters such as the energy density (fluence), pulse duration ($\tau_p$), wavelength, polarization, laser repetition rate [54]. The material properties that affect the surface temperature and nature of evaporation are the thermal diffusivity ($D_t$) and optical absorption coefficient ($\alpha_l$) at the laser wavelength. During initial stages of the laser-target interaction, thermal energy is absorbed into a thin layer on the surface of the target, and then diffuses into the target during the laser pulse duration. The depth of the heated volume of material is given by the thermal diffusion length ($l_d$) [55]:

$$l_d = \sqrt{2D_t \tau_p}$$  \hspace{1cm} (1.20)

where the thermal diffusivity ($D_t$) of the material is given by:

$$D_t = \frac{\kappa}{\rho C_p}$$  \hspace{1cm} (1.21)

Figure 1.10. A diagram of the excimer laser energy (i) absorption by the target material and initiation of ablation and (ii) continued target ablation and fractional plasma absorption of the laser pulse.
where $\kappa$ is the thermal conductivity, $\rho$ is the material density, and $C_p$ is the heat capacity.

If the thermal diffusion length $l_d << a_i^{-1}$ then the heated depth $d_H \approx a_i^{-1}$, or if $l_d >> a_i^{-1}$ then $d_H \approx l_d$ [55] (Figure 1.10b). Low diffusivity and high absorption, results in high peak temperatures and concentration of thermal energy at the surface, which are good for congruent evaporation. The transfer of energy occurs within a few picoseconds, then heating of the absorption layer will begin. Vaporization of the absorption depth will begin with a timeframe on the order of 100 ps from the arrival of a 20 ns laser pulse duration [54].

Figure 1.11. The evolution of the laser-target interaction. The (a) The unablated target, (b) laser pulse arrival, rapid target surface heating, and plasma initiation, (c) pulse continuation, pulse absorption into the expanding plasma, and increased surface heating and propagation into the target, (d) pulse termination, hydrodynamic plasma expansion, and rapid target cooling, and (e) ideal return of the target to the initial state.
At sufficiently high laser fluence, a plasma is formed in the vapor over the target area irradiated by the incident laser pulse. The interaction of this plasma with the remainder of the laser pulse and evaporation source, strongly affects the nature of the evaporation and energy coupling to the target surface. A general feature of pulsed laser ablation plasmas, or plumes, is the high ion and electron temperatures on the order of several thousand Kelvin, and the high degree of ionization [54]. When this plasma is dense enough it will absorb laser radiation directly by inverse Bremsstrahlung process [56] and the plasma absorption coefficient ($\alpha_v$) is given by:

$$\alpha_v = 3.69 \times 10^3 \left( \frac{Z_c^3 n_i^2}{T^{1/2} \nu^3} \right) \left[ 1 - e^{\left( \frac{\hbar \nu}{k_T \nu^2} \right)} \right]$$

(1.22)

where $Z_c$ is the average charge in the plasma of ion density $n_i$, at temperature $T$, and laser frequency $\nu$. Also, $n_e$, $q$, $m_e$, are the electron density, electronic charge, and electron mass, respectively. This absorption increases the plasma temperature and shields the evaporating surface from laser radiation so that the evaporation enters a self-regulating regime. Radiant heating from the plasma, and plasma impingement, further heats the surface, increasing the energy coupling efficiency to the material (Figure 1.10c).

In instances where a plasma is produced, the wavelength of irradiation determines the fractional absorption of the beam by the plasma. The plasma resonant frequency ($v_p$) is given by:

$$v_p = \left( \frac{4 \pi q^2}{m_e} \right)^{1/2}$$

$$v_p = 8.9 \times 10^3 (n_e)^{1/2}$$

(1.23)
A ratio of $v_l/v_p \approx 1$ is necessary in order for substantial absorption to occur in the plasma, where $v_l$ is the laser frequency [56, 57]. A laser pulse optical frequency greater than the plasma frequency, $v_l > v_p$, results in the laser energy predominately penetrating the plasma and continuing to interact with the target surface. If $v_p > v_l$ then proportionally more of the laser energy will be reflected from the plasma. The number and density of the excited and ionized atoms is a strong function of laser fluence for evaporation. Typical values of the charge density are $n_e = 10^{19} - 10^{20} \text{ cm}^{-3}$ for plasmas generated by PLA. This will lead to critical plasma frequency values in the range of $3 \times 10^{13}$ to $9 \times 10^{13} \text{ s}^{-1}$.

Formation of the plasma and its subsequent hydrodynamic expansion are the origin of the high kinetic energy, and ionized and excited neutral species, and their impingement on the film growth surface, which play important roles in the nucleation, structure, and growth of thin-films [58]. The plasma will produce species with high kinetic energies ranging between 1 eV and more than 100 eV [59, 60]. Particle energies in the 10 to 1000 eV range are sufficient to break atomic bonds, cause thermal spikes, generate subsurface vacancies and displacement of atoms, and enhance surface diffusivity of the adsorbed atoms. These mechanisms generally improve the film microstructure and morphology in a manner similar to ion-assisted deposition [61]. They can also cause damage to the substrate and film as with ion etching [62]. Lower substrate temperatures can be used in pulsed laser deposition due to enhanced surface mobility caused by energetic bombardment during deposition [54]. For example, epitaxial germanium film growth was possible at 300 °C using PLD while for molecular-beam epitaxy (MBE), temperature in excess of 700 °C are required [51].
PLD stands out as perhaps the most promising deposition choice for a broad range of materials. Reliable congruent transfer of material from bulk to film is possible, the energy range of the impinging particles promotes surface diffusion while avoiding bulk damage, the species are often activated either as ions or excited neutrals which facilitate associative chemistry on the growing film, and virtually all materials can be ablated [54].

1.3. Summary

The pursuit of improved performance of TE materials is motivated by energy production and conservation issues. TE materials with complex structures and intrinsically low thermal conductivity such as type-I clathrates are promising candidates for investigation. In addition, the enhanced performance of TE structures composed of thin-films is of interest. TE devices composed of thin-films may be appropriate for small-scale electronic and optoelectronic applications where small heat loads or low level of power generation are more appropriate [71]. The advantages of PLD are ideal for in-situ growth of such complex multi-component materials such as type-I clathrate. Based on the results obtained, this will help establish a basic understanding of film growth of complex structures, and to date the quantity of reports on the production and characterization of any type-I clathrate thin-films are extremely limited [72].

1.4. Outline of Dissertation

The thin-film growth and characterization of the novel thermoelectric material type-I clathrate Ba₈Ga₁₆Ge₃₀ deposited by pulsed dual-laser ablation was studied through the following investigations. The surface modification of the polycrystalline target by
pulsed laser ablation techniques was investigated through surface morphology and composition studies (Chapter 3). The optical emission and expansion of the vaporized material plume in transit to the substrate was studied by in-situ optical diagnostics (Chapter 4), and a hydrodynamic model of the plasma expansion was investigated (Chapter 5) to determine plasma temperatures of the ablated material. The resultant films were studied for the structure and electric transport properties (Chapter 6). A comprehensive summary of these results and a brief discussion of future directions will be presented (Chapter 7).
CHAPTER 2:
DUAL-LASER ABLATION

For certain applications, there remains an obstacle with PLD despite its advantages. Some materials when used with PLD produces fine particulates, ranging in size from microns down to submicron dimensions. Particulates generated by pulsed laser ablation can be distinguished by whether the original material when ejected from the target is in the solid, liquid, or vapor state [55]. The size of particulates formed from the vapor state tends to be in the nanometer range and may be spherical or polyhedral in shape. The shape of particulates formed from liquid ejecta tend to be spherical and in the sub-micron to micron size range. Particulates formed from solid ejecta are also in the micron size range and tend to be irregularly shaped. There are multiple sources of particulate generation: (1) dislodged fragments from pits and micro-cracks due to laser-induced thermal and mechanical shock; (2) rapid expansion of trapped gas beneath the target surface during laser irradiation causing forcible ejection of material; (3) splashing of the molten layer caused by the presence of a subsurface superheated layer or from laser-induced rapid surface evaporation; and (4) condensation from vapor species due to supersaturation observed with high ambient gas pressure [55, 53]. Particulates incorporated into the film degrade its properties and the tolerance for particulates is application specific as well as dependent on their size and density. Considering an electronic thin-film component with a typical width of 10 µm, a particulate density of less
that 1 per 100 µm² may be desirable [55].

A number of techniques exist to eliminate particulates. A high-quality, high-density target can minimizes the problem for some materials, and other active and passive techniques have been developed to filter out the heavy particulates [52]. A simple approach to reduce the number of particulates is to reduce the laser power density to below the threshold level that causes the splashing of the molten layer, also by increasing the spot size [63, 55]. Rotating vane velocity filters can be used to stop the slow moving massive particles (~1-10 cm/ms), but let the fast atomic and molecular evaporants through (~1 cm/µs) [64, 55]. Other techniques involve gas-dynamic separation [62], “off-axis” deposition [65], and substrate biasing [66] to separate massive particles from the vapor plume [55].

![Diagram of the pulsed dual-laser ablation system](image)

**Figure 2.1.** A diagram of the pulsed dual-laser ablation system. The system can be operated in either excimer-only single-laser or dual-laser mode.
A modified approach for particulate reduction is employing a second pulsed laser to control particulate production (Figure 2.1). The plume absorption of the second laser pulse, to heat the plume formed by the first laser, evaporates the ejected matter in the plume. This pulsed dual-laser ablation technique utilizes spatial overlap of two laser pulses of different wavelengths on the target surface. The ejection of particulates is essentially eliminated with use of a suitable temporal delay between the two laser pulses (Figure 2.2). Additionally, this technique enhances the evaporated species kinetic energy and ionization in the laser-ablated plume by enhanced plume excitation. This allows the reduction of the substrate temperature for epitaxial film growth as a result of the increased mobility on the substrate due to enhanced plume excitation.

![Figure 2.2](image_url)

**Figure 2.2.** Oscilloscope traces of the temporal synchronization of the (UV) excimer laser pulse and the (IR) CO_2 laser pulse. The *p-p* delay (peak-to-peak) is shown relative to the peak of the excimer laser pulse.
Figure 2.3. Evolution of the laser-target interaction for dual-laser ablation. (a) CO$_2$ laser pulse arrival and on-set of surface melt, (b) synchronized arrival of the excimer laser pulse to interact with the pre-melt zone, initiate evaporation and plasma formation, and dual-laser plasma absorption, and (c) termination of the excimer pulse, and continued plasma absorption of the CO$_2$ laser pulse, increasing plasma temperature and expansion.
During ablation (Figure 2.3) using the dual-laser process the IR CO\textsubscript{2} laser pulse arrives at the target first and begins to heat up the material (Figure 2.3a). When the UV excimer laser (KrF) pulse arrives at the same spot on the target that has been heated just above the melting point by the CO\textsubscript{2} laser pulse, it interacts with a smooth molten layer of the material (Figure 2.3b). The molten material lacks any cracks and loose particles that could produce particulate ejection [53]. The plasma plume formed at the target surface will interact with the remaining part of the CO\textsubscript{2} laser pulse to heat the plume to a higher temperature, through the inverse Bremsstrahlung process (eq. 1.22) that would re-evaporate any submicron particles remaining in the plume (Figure 2.3c). This dual-laser deposition process reduces the particulates without losing any of the basic advantages that makes pulsed laser deposition appealing for thin film deposition [47-49, 67-69]. Material ablation by synchronized dual-lasers is a promising technique to simultaneously minimize both particulates and the narrow angular distribution problem of standard single-laser PLD [70]. This dual-laser ablation technique has been successfully employed in the control of Pb depletion in PZT (PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3}) films [125], and film growth of Y\textsubscript{2}O\textsubscript{3} [126, 132], Zn [127], ZnO [126, 128, 130, 131], diamond-like carbon [129], multi-component films of CuIn\textsubscript{0.75}Ga\textsubscript{0.25}Se\textsubscript{2} [131], and Er-doped Y\textsubscript{2}O\textsubscript{3} [133].

The implementation of the dual-laser system ultimately involves the relationship between the two laser pulses at the target surface and the qualities of the material. The effect of laser-target interactions of each laser individually will guide selection of promising fluences for each laser when used in combination. Generally, the applicable fluence of the excimer laser is greater than the threshold fluence but less than the optimum fluence required during the standard single-laser ablation method. The choice of
the CO₂ laser energy for a particular material is a fluence that produces surface melting without causing significant material removal through ablation. The two lasers then require temporal synchronization such that the CO₂ laser pulse arrives at the target first to initiate surface melting, followed by the arrival of the excimer laser pulse at on-set of the melt, see Figure 2.2. The proper coupling of the infrared (IR) CO₂ laser energy with the ultraviolet (UV) excimer laser generated plasma results in ionic enhancement and increased kinetic energy of the evaporated material may allow even lower substrate temperatures to be used as compared to standard single-laser PLD due to the enhanced surface mobility caused by energetic bombardment during deposition [68].

2.1. Description of the Pulsed Dual-Laser Ablation System

The concept of single-laser PLA, or PLD, was introduced Chapter 1.2. The dual-laser ablation system, shown in Figure 2.1, can be operated in either single-laser or dual-laser modes of operation. The evacuation of deposition chamber is performed by a roughing pump and turbo molecular pump in series, to the upper micro-torr range, then by a closed cycle cryo-pump, to the 10⁻⁷ torr range. The substrate heater is a stainless steel block internally heated by a 600 watt halogen bulb, with a temperature range of room temperature (26 °C) to 700 °C. The substrate temperature is monitored by a K-type thermocouple with the tip in thermal contact by conductive silver paste to the face of the heater block. The substrates are located adjacent to the thermocouple tip and fixed to the heater block with conductive silver paint to improve thermal contact. The substrate temperature was referred to, and recorded as, the surface temperature of the heater block. The target-to-substrate distance was typically maintained at 4 cm on-axis to the laser-
target interaction site. The laser utilized during single-laser ablation is a UV KrF excimer laser with a pulse full-width-half-maximum (FWHM) duration of 28 - 56 ns, emitting a wavelength of 248 nm. During experiments using dual-laser ablation the second laser is a far IR CO2 laser with a pulse FWHM of 250 ns, emitting a wavelength of 10.6 μm. The pulses from the two lasers are synchronized through the use of delayed triggering from an inductive-pickup of the CO2 laser discharge. The reported laser fluences are measured at the target surface, accounting for losses through the optical path(s) of the laser pulse. Losses occur at optical elements such as the mirrors, lenses, and chamber windows; there was 70.3 % transmission of the excimer laser pulse, and 86.9 % transmission of the CO2 laser pulse, to the target.

2.1.1. Dual –Laser System Parameters

The dual-laser system described in Figure 2.1 is initiated by the internal trigger of the CO2 laser (Figure 2.4a). An inductive-pickup of the CO2 laser capacitor discharge (Figure 2.4b) is used to trigger the digital delay generator (DDG) $t_0$ signal (Figure 2.4c) to trigger the excimer laser. The temporal delay between the excimer laser output pulse (Figure 2.4d) and the CO2 laser output pulse (Figure 2.4e) is detected by the UV and IR detectors (Figure 2.1) and monitored on a fast oscilloscope, 1 gigi-samples per second, and regulated by the excimer laser triggering delay set by the DDG.

There are innate properties of the lasers that affect the internal delay between their trigger and output. These properties include the level of the high-voltage (HV) applied to the discharge capacitors, the ratio of the gas mixtures, and for the CO2 laser specifically, the output coupler reflection (OC) and laser cavity geometry. Typically, it is desired to
have the excimer laser output occur as early as possible, and the CO₂ laser pulse to occur as late as possible, while still maintaining the quality of the laser pulse. This allows the $pp$ delay to be controlled over a large range by the DDG. The temporal delay is referenced relative to the peak of the excimer laser pulse (0 ns), called the peak-to-peak delay ($pp$

![Figure 2.4](image-url)

**Figure 2.4.** The time-line of component synchronization for the dual-laser ablation system. The $t_0$ trigger to initiate the dual-laser pulse cycle is the (a) CO₂ laser internal trigger, followed by the (b) CO₂ laser capacitor discharge, which triggers the (c) digital delay generator (DDG) $t_0$ signal to trigger the excimer laser, followed by the (d) excimer laser output pulse, and (e) the CO₂ laser output pulse.
delay). If the peak of the CO₂ laser pulse occurs after the peak of the excimer laser pulse, the \( p-p \) delay is positive (+), and a CO₂ laser peak before the excimer pulse would be negative (-). The typical \( p-p \) delay range is limited to approximately +250 ns by the CO₂ laser gain build-up time, and is essentially unlimited in the negative \( p-p \) direction. For practical purposes, a negative \( p-p \) delay greater than -50 ns would cause undesired ablation by the CO₂ laser pulse energy, and not allow enough remaining energy in the CO₂ laser pulse to interact with the excimer laser-generated plasma. Laser pulse quality is evaluated by uniformity of the energy distribution across the laser spot area, and the jitter. Energy distribution becomes less uniform at low laser energy. Jitter is a measure of the fluctuations of the temporal positions of pulses, as illustrated in Figure 2.5. Previous experiment reports have demonstrated that precise synchronization of the two laser pulses

![Figure 2.5](image-url)

**Figure 2.5.** Detail of the cumulative oscilloscope traces of the excimer and CO₂ laser pulses to illustrate the 16 ns jitter of the CO₂ laser pulses relative to the excimer laser pulses. The jitter is measured between the minimum and maximum occurrence of the full-width at half-maximum (FWHM) of the laser pulses.
to within tens of nanoseconds is crucially important for the particulate-free deposition of thin films [67, 69] and excessive jitter will adversely affect pulse-to-pulse synchronization. Laser pulse jitter is affected by the HV, gas mixture, OC, and CO2 laser cavity geometry. Greater levels of HV will reduce jitter, depleted gas mixture will increase jitter, high OC reflection decreases jitter, and longer laser cavity length increases jitter. A summary of the laser parameters effect on the laser output is given in Table 2.1. The listed parameters are the high-voltage applied to the discharge capacitors (HV), the gas mixture ratio, the reflection of the CO2 laser output coupler (OC), and cavity length of the CO2 laser.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Effect on laser output</th>
<th>Energy</th>
<th>Delay</th>
<th>Jitter</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV</td>
<td>High</td>
<td>Increase</td>
<td>Decrease</td>
<td>Decrease</td>
<td>Decrease</td>
<td>Increase</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>Decrease</td>
<td>Increase</td>
<td>Increase</td>
<td>Decrease</td>
<td>Decrease</td>
</tr>
<tr>
<td></td>
<td>Optimum</td>
<td>Increase</td>
<td>Decrease</td>
<td>Decrease</td>
<td>Decrease</td>
<td>Negligible</td>
</tr>
<tr>
<td>Gas Mixture</td>
<td>Depleted</td>
<td>Decrease</td>
<td>Increase</td>
<td>Increase</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>Increase</td>
<td>Decrease</td>
<td>Decrease</td>
<td>Decrease</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>Decrease</td>
<td>Increase</td>
<td>Increase</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td>OC Reflection</td>
<td>High</td>
<td>Negligible</td>
<td>Increase</td>
<td>Increase</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>Negligible</td>
<td>Decrease</td>
<td>Decrease</td>
<td>Negligible</td>
<td></td>
</tr>
</tbody>
</table>

A summary of the laser parameters effect on the laser output is given in Table 2.1. The listed parameters are the high-voltage applied to the discharge capacitors (HV), the gas mixture ratio, the reflection of the CO2 laser output coupler (OC), and the cavity length of the CO2 laser. The effects on the laser output by changing these parameters are evaluated by the pulse energy, delay, jitter, and duration ($τ_p$). Adjusting one parameter to achieve a desired output effect generally requires compensation by other parameters. Therefore, a compromise of the parameters is established to have control over the range of values desired.
2.1.2. CO₂ Laser Parameters

It was found that configuring the CO₂ laser with a ZeSe Brewster window attached to an extension tube yielded the best results for achieving a consistent and uniform laser pulse with a practical energy density range required for experimental purposes. Placing the window as far or farther (20.75 inches, on center) from the end of the electrodes as the gold back mirror’s distance (12 inches), kept the ZnSe window from becoming damaged due to sputtering from ionized gas within the laser gas cavity (Figure 2.6). The final cavity length was 161.8 cm, which was the longest length which could be accommodated to maximize the delay and also allow ample working space for adjustments and maintenance. An 80% reflectivity and 20 meter curvature germanium output coupler was chosen which produced approximately 550 mJ of energy at a HV of 36.5 kV, while providing a delay of 975-1310 ns (Appendix K). The spatial filter was completely opened for maximum power output and the output coupler was adjusted for 6-2 multi-mode. A standard gas premix was used for the CO₂ laser, see Table 2.2, and was

![Schematic diagram of the CO₂ laser with the ZnSe Brewster window extension tube and Ge output coupler.](image)

**Figure 2.6.** Schematic diagram of the CO₂ laser with the ZnSe Brewster window extension tube and Ge output coupler.
flowed constantly in order to maintain consistent energy output. The laser applied HV was maintained at 30 kV or greater to minimize the jitter.

Table 2.2. The CO\textsubscript{2} laser gas premix used during dual-laser ablation.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mix Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>4</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>12</td>
</tr>
<tr>
<td>He</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.1.3. Excimer Laser Parameters

The cavity length and output coupler of the excimer laser were not modified from the original manufactures configuration. As shown in Figure 2.7a-b, as the HV is increased the output energy increases, and as the energy is increased, the delay and jitter decrease. These are desirable characteristics; however, the output energy is too high for the required dual-laser conditions. The gas mixture was then intentionally depleted by manually injecting the neon buffer gas into the laser cavity while maintaining required 3000 mbar cavity pressure. This buffer injection results in decreased energy output at elevated HV settings without significantly increasing the jitter or delay.
2.2. Summary

Through proper configuration of the dual-laser system it was possible to achieve the desired output conditions. CO\textsubscript{2} and excimer laser fluences as high as 3 J/cm\textsuperscript{2} for each laser could be achieved, with a \textit{p-p} delay range of -50 to 200 ns, and typical dual-laser jitter of 16 ns with 8 ns capability. This degree of flexibility provides a versatile system for experimental investigations of pulsed laser ablation.

\textbf{Figure 2.7.} Output characteristics of the excimer laser after a new fill, the (a) output delay and (b) pulse jitter relative to the trigger pulse, as a function of the output energy.
CHAPTER 3:
INVESTIGATION OF TARGET SURFACE MODIFICATION
BY PULSED LASER ABLATION

In order to produce high quality thin films by PLD with basic properties such as broad area, smooth topography, uniform distribution, and stoichiometric deposition, it is essential to gain an understanding of the interaction between the focused laser pulse and the target surface. Insight into this laser-target interaction can be gained through investigations of the target surface modification by the high power, pulsed laser ablation of the material of interest. Stoichiometric deposition is dependent on congruent evaporation of the laser irradiated target, and to achieve this, the entire heated volume (the laser irradiated spot area and heated depth) must be vaporized during each laser pulse. However, if a high percentage of the molten material is left behind, phase segregation and re-crystallization will take place [50]. Factors relevant to surface modification follows: (i) the maximum temperature reached in the solid and the melt depth, increase with laser fluence, (ii) the thermal pulse penetrates deeper into solids with low absorption coefficients and high thermal conductivities, and (iii) shorter pulse lengths produce higher melting and solidification velocities [50, 73]. The more intrinsic aspects of the laser/solid interaction are dependent on the important laser parameters; pulse width, wavelength, and fluence (energy density). It is typically desirable to have the pulse width on the order of nanoseconds or shorter, for longer pulse widths, the energy
delivered by the laser is carried away by thermal conduction to a significant extent. Use of a KrF excimer laser (248 nm) as the primary laser for ablation, results in pulse widths in the range of 20 to 60 ns. There are few restrictions placed on the targets used in a pulsed laser deposition (PLD) system. Successful deposition can be made from pressed powders, sintered pellets, cast material, single crystals, and metal foils. The main differences between these different target morphologies are in the nature of the target erosion, and the generation of particulates. A general guide is that high-density and highly homogenous targets yield the best films [74].

Table 3.1. Crystallographic and transport properties for single crystal type-I clathrate Ba$_8$Ga$_{16}$Ge$_{30}$ at room temperature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td></td>
<td></td>
<td>B$<em>8$Ga$</em>{16}$Ge$_{30}$</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>K</td>
<td>295</td>
<td></td>
</tr>
<tr>
<td>Formula Weight</td>
<td></td>
<td>(g/mol)</td>
<td>4391.94</td>
<td>15</td>
</tr>
<tr>
<td>Space Group</td>
<td></td>
<td></td>
<td>Pm-3n</td>
<td>15</td>
</tr>
<tr>
<td>Lattice Parameter</td>
<td>$a$</td>
<td>Å</td>
<td>10.767(10)</td>
<td>15</td>
</tr>
<tr>
<td>Volume</td>
<td>$V$</td>
<td>Å$^3$</td>
<td>1248.2(2)</td>
<td>15</td>
</tr>
<tr>
<td>Atoms/Unit Cell</td>
<td>$Z$</td>
<td></td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>Density</td>
<td>$\rho_{\text{calc}}$</td>
<td>g/cm$^3$</td>
<td>5.843</td>
<td>15</td>
</tr>
<tr>
<td>Linear Absorption Coefficient</td>
<td>$\alpha_l$</td>
<td>mm$^{-1}$</td>
<td>32.383</td>
<td>15</td>
</tr>
<tr>
<td>Melting Point</td>
<td></td>
<td>°C</td>
<td>963 ± 5</td>
<td>18</td>
</tr>
<tr>
<td>Seebeck Coefficient</td>
<td>$\alpha$</td>
<td>µV/K</td>
<td>50</td>
<td>18</td>
</tr>
<tr>
<td>Carrier Concentration</td>
<td>$n$</td>
<td>cm$^{-3}$</td>
<td>$\sim 10^{21}$</td>
<td>18</td>
</tr>
<tr>
<td>Mobility</td>
<td>$\mu$</td>
<td>cm$^2$/V$\cdot$s</td>
<td>10-15</td>
<td>18</td>
</tr>
<tr>
<td>Band gap</td>
<td>$E_g$</td>
<td>eV</td>
<td>0.89</td>
<td>19</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>$C_p$</td>
<td>J/g$\cdot$K</td>
<td>0.3065</td>
<td>4</td>
</tr>
<tr>
<td>Lattice Thermal Conductivity</td>
<td>$\kappa_L$</td>
<td>W/m$\cdot$K</td>
<td>1.9-2.1</td>
<td>4</td>
</tr>
</tbody>
</table>

in the range of 20 to 60 ns. There are few restrictions placed on the targets used in a pulsed laser deposition (PLD) system. Successful deposition can be made from pressed powders, sintered pellets, cast material, single crystals, and metal foils. The main differences between these different target morphologies are in the nature of the target erosion, and the generation of particulates. A general guide is that high-density and highly homogenous targets yield the best films [74].
Reported values for properties of single-crystal type-I clathrate Ba$_8$Ga$_{16}$Ge$_{30}$ are given in Table 3.1. The band gap of Ba$_8$Ga$_{16}$Ge$_{30}$ is 0.89 eV, and since it is desirable to have the photon energy ($E_\lambda$) of the laser greater than the band gap of the material being ablated (equation 1.19), then the KrF excimer laser (5.00 eV) will satisfy this parameter (Table 3.2). This will allow lower energy densities for ablation. Whereas, the CO$_2$ laser with 10.6 µm wavelength ($E_\lambda = 0.117$ eV) would not be an appropriate ablation source.

Based on the material properties values (Table 3.1) for the thermal conductivity ($\kappa_L$), density ($\rho$), and heat capacity ($C_p$), the calculated thermal diffusivity ($D_T$) is 1.06 – 1.17 mm$^2$/s. From previously reported excimer laser ablation of Ba$_8$Ga$_{16}$Ge$_{30}$ using fluences of 1 – 3 J/cm$^2$ [6], the laser pulse duration ($\tau_p$) is 30 – 43 ns. The calculated thermal diffusion length ($l_d$) is then 0.25 – 0.32 µm. The linear absorption coefficient ($\alpha_l$) of Ba$_8$Ga$_{16}$Ge$_{30}$ is 32.383 mm$^{-1}$ [76] and since $l_d << \alpha_l^{-1}$ where $\alpha_l^{-1} = 30.88$ µm then the
heated depth is $d_H \approx \alpha v^{-1} \approx 30.88 \, \mu m$ [55]. Since $a_d >> l_d$, the complete volume is vaporized during a high energy laser pulse, preventing any phase segregation. This leads to congruent evaporation; however, at low laser pulse energies the entire volume does not reach the boiling point of the material and this leaves the low volatile material behind leading to non-stoichiometric evaporation [50].

During dual-laser ablation, the majority of the IR CO\textsubscript{2} laser pulse is absorbed into the excimer laser-generated plasma since the absorption coefficient ($\alpha_v$), equation 1.22, is proportional to $v^{-3}$ or $\lambda^3$, where the absorption is much stronger for the longer wavelength CO\textsubscript{2} laser than the excimer laser radiation. Then, by the inverse Bremsstrahlung process [56], the target is screened from further ablation by the relatively long CO\textsubscript{2} laser pulse. In addition, the absorbed CO\textsubscript{2} laser energy causes intense heating of the plasma and can evaporate the submicron particulates passing through the plasma and at the same time enhance the kinetic energies of the plume species [47]. Also, since the wavelength of irradiation determines the fractional absorption of the beam by the plasma, as compared to the plasma frequency ($v_p$), equation 1.23. When $v_i/v_p \approx 1$, substantial absorption to the plasma occurs, and given typical values of the charge density are $n = 10^{19} - 10^{20} \, \text{cm}^{-3}$ for plasmas generated by PLA, then the critical plasma frequency values will be in the range of $3 \times 10^{13}$ to $9 \times 10^{13} \, \text{s}^{-1}$. As compared to the optical frequency of the KrF excimer laser, $v_{UV} = 1.2 \times 10^{15} \, \text{s}^{-1}$, and the CO\textsubscript{2} laser, $v_{IR} = 2.8 \times 10^{13} \, \text{s}^{-1}$, the CO\textsubscript{2} laser frequency is near ideal for absorption into the plasma.

Due to the low thermal conductivity and thermal diffusion length, the heated volume of Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} will be small. These results, combined with the short KrF excimer laser pulse duration, are good conditions for congruent evaporation at relatively
moderate ablation fluences. Under dual-laser ablation, absorption of CO₂ laser pulse energy into the excimer laser-generated plasma will contribute to increased plasma temperatures, leading to enhanced kinetic energy and ionization. Investigation of the Ba₈Ga₁₆Ge₃₀ target surface modification by pulsed laser ablation will lead to understanding of conditions which are conducive to congruent evaporation and contribute to growth of high-quality thin films.

### 3.1. Ba₈Ga₁₆Ge₃₀ Target Properties

The Ba₈Ga₁₆Ge₃₀ type I clathrate material used for the packed-powder laser ablation target was synthesized at the Novel Materials Laboratory at the University of South Florida, Physics Department [77]. The material was prepared by mixing stoichiometric quantities of the high purity elements Ba (99%, Aldrich), Ga (99.9999%, Chameleon), and Ge (99.99%, Alfa Aesar). The powder mixture was placed in a pyrolytic boron nitride crucible, and sealed in a fused quartz ampoule under high purity nitrogen gas at a pressure of 2/3 atmosphere. To form Ba₈Ga₁₆Ge₃₀, the mixture was heated at 1 °C/min, held at 1000 °C for 24 hours, and then cooled at a rate of 2 °C/min; the total synthesis time was approximately 48 hours. The resulting product consisted of ingots possessing a metallic luster, which was then ground to 325 mesh, approximately 45 µm. The density of the material was higher than 95% of the theoretical X-ray density (5.843 g/cm³ [78]), as analyzed by powder X-ray diffraction (XRD). The clathrate powder was uni-axial cold die pressed in a 1.25 inch diameter die with a load of 27.4 × 10³ lb/in² and maintained for six hours. The compacted bulk density of the final target was 4.19 ± 0.07 g/cm³, which is 71.8% ± 1.1% of the theoretical density.
The indexed powder XRD pattern of the cold-pressed target is shown in Figure 3.1, and the corresponding indices are given in Table 3.3. The XRD pattern was indexed to a cubic unit cell structure with space group Pm-3n. The diffraction pattern displays peaks which are characteristic of type-I clathrates and are in good agreement with those reported for Ba₈Ga₁₆Ge₃₀ [78, 79]. The XRD spectrum indicates trace amounts of the impurity phase diamond structured germanium found at 27.3° 2Θ, which has been observed in other work [34, 80, 81].

Figure 3.1. The normalized, indexed, powder XRD pattern for the cold-pressed Ba₈Ga₁₆Ge₃₀ type-I clathrate target.
The samples of the cold-pressed target were flat-polished to a surface roughness of 10.1 ± 9.6 nm (RMS 13.9 nm) and the chemical composition was analyzed by energy dispersive x-ray spectroscopy (EDS) (JEOL) at 20 keV, as given in Table 3.4. The results

<table>
<thead>
<tr>
<th>2θ (deg)</th>
<th>Intensity (%)</th>
<th>(hkl)</th>
<th>d (Å)</th>
<th>Note</th>
</tr>
</thead>
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<tr>
<td>27.27</td>
<td>13.1</td>
<td></td>
<td>3.268</td>
<td>Ge</td>
</tr>
<tr>
<td>28.66</td>
<td>26.0</td>
<td>(222)</td>
<td>3.112</td>
<td></td>
</tr>
<tr>
<td>29.85</td>
<td>35.8</td>
<td>(320)</td>
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<tr>
<td>30.99</td>
<td>100.0</td>
<td>(321)</td>
<td>2.883</td>
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<tr>
<td>33.21</td>
<td>15.6</td>
<td>(400)</td>
<td>2.696</td>
<td></td>
</tr>
<tr>
<td>34.27</td>
<td>15.4</td>
<td>(410)</td>
<td>2.615</td>
<td></td>
</tr>
<tr>
<td>35.25</td>
<td>7.5</td>
<td>(411)</td>
<td>2.544</td>
<td></td>
</tr>
<tr>
<td>37.26</td>
<td>8.9</td>
<td>(420)</td>
<td>2.411</td>
<td></td>
</tr>
<tr>
<td>45.28</td>
<td>15.4</td>
<td>(520)</td>
<td>2.001</td>
<td>Ge + Ba₈Ga₁₆Ge₃₀</td>
</tr>
<tr>
<td>47.66</td>
<td>7.3</td>
<td>(440)</td>
<td>1.907</td>
<td></td>
</tr>
<tr>
<td>49.17</td>
<td>29.3</td>
<td>(530)</td>
<td>1.851</td>
<td></td>
</tr>
<tr>
<td>49.99</td>
<td>13.4</td>
<td>(531)</td>
<td>1.823</td>
<td></td>
</tr>
<tr>
<td>50.73</td>
<td>17.9</td>
<td>(600)</td>
<td>1.798</td>
<td></td>
</tr>
<tr>
<td>52.24</td>
<td>38.0</td>
<td>(611)</td>
<td>1.750</td>
<td>Ge + Ba₈Ga₁₆Ge₃₀</td>
</tr>
<tr>
<td>53.68</td>
<td>10.1</td>
<td>(620)</td>
<td>1.706</td>
<td></td>
</tr>
<tr>
<td>54.45</td>
<td>6.4</td>
<td>(540)</td>
<td>1.684</td>
<td></td>
</tr>
</tbody>
</table>

The powder XRD indices for the cold-pressed Ba₈Ga₁₆Ge₃₀ type-I clathrate target. The XRD source is Cu Kα.

Table 3.4. Composition and Ga/Ge atomic ratio of the Ba₈Ga₁₆Ge₃₀ type-I clathrate cold-pressed target determined by EDS analysis.

| Atomic % |  |
|----------|--|---|---|---|
|          | Ba | Ga | Ge | Ga/Ge |
| Stoichiometric | 8.0 | 16.0 | 30.0 | 0.533 |
| Target    | 8.5 ± 0.2 | 15.6 ± 0.6 | 30.0 ± 0.6 | 0.53 ± 0.03 |
were normalized to the average Ge\textsubscript{30} atomic percent (at.\%) composition. The target material was found to appear slightly Ba rich, as compared to the stoichiometric 8:16:30 ratio. However, the Ga/Ge ratio of 0.53 \pm 0.03 is consistent with the intrinsic material.

3.2. Experimental Details

In order to study the effect of the surface modification at the laser-target interaction site by the pulsed-laser ablation processes, the Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} packed-powder target was re-surfaced and polished with super-fine ISO P1200 grit (15.3 \(\mu\)m average particle diameter) sand paper (see Appendix B) to provide a smooth target surface which has not been processed by laser ablation (Figure 3.2). The target was then sprayed with pressurized dry nitrogen gas to remove loose particles. The target was mounted in the appropriate target-holder and installed in the vacuum chamber.

![Figure 3.2. SEM image of the coarse polished (529 nm rms) Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} type-I clathrate cold-pressed target. Approximately 315×315 \(\mu\)m viewing area.](image)

The target was kept stationary during each trial so the laser pulse could interact with the same region for a given laser fluence and number of pulses. This reduced the
experiment duration and more importantly, the overall erosion of the target. For subsequent trials, the next laser-impingement site was changed to a clean, un-ablated location either by moving the laser spot location by vertical translation of the focusing, or rotating the target. The process was repeated for the next number of repetitions or laser fluence. The focused laser spot size at the target surface (Figure 3.3), was maintained at 2.0 mm wide by 3.0 mm high for each laser fluence, by adjusting the laser focusing lens(es).

Figure 3.3. Diagram of the laser spot size at the laser-target interaction site.

The vacuum chamber was evacuated to $10^{-6}$ Torr for this investigation. The focused laser pulse was impinged onto target surface locations for 1, 10, 100, and 1000 counts. The UV KrF excimer laser fluence was varied to 1, 2, 3, 4, and 5 J/cm$^2$. The IR CO$_2$ laser fluence was varied to 0.3, 0.6, 1.3, 1.8, 2.0, and 2.4 J/cm$^2$. The surface morphology and composition of the laser-target interaction sites were then examined for
morphological and compositional changes by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively.

A photograph of the Ba$_8$Ga$_{16}$Ge$_{30}$ target after various UV laser fluences and repetitions (Figure 3.4), displays the result of the accumulated laser impingement. Figure 3.5 shows the typical layout of the SEM and EDS analysis sites. SEM observations were conducted at 30X to 30000X magnifications to determine appropriate representation of the morphology of the surface. It was concluded that 300X magnification (approximate scan area of 315 × 315 µm) is representative of the laser-target interaction area. EDS was performed and at four adjacent locations at each site, the average and standard deviation these locations were reported. Each interaction site was compared to a bare, un-ablated region of the target surface for surface morphology and stoichiometry.

![Figure 3.4](image_url)

**Figure 3.4.** Photograph of the Ba$_8$Ga$_{16}$Ge$_{30}$ target with various laser interaction sites at fluences of 1 to 5 J/cm$^2$ and repetitions of 1, 10, 100, and 1000 pulses.

The results of the single-laser, excimer only and CO$_2$ only, laser-target interactions will determine the laser fluence combination to be used for the dual-laser ablation investigations.
3.3. Investigation of the Excimer Laser - Target Interaction

SEM images are shown for UV KrF excimer only, laser-target interaction sites for fluences of 1, 2, 3, 4, and 5 J/cm² at cumulative pulses or 10, 100, and 1000 pulses per site, respectively (Figure 3.6a and b). The surface modification can be compared to the un-ablated target region shown in Figure 3.2. It was observed that practical ablation did not occur with an excimer laser fluence of 0.5 J/cm². This establishes that the ablation threshold ($F_T$) is approximately 0.5 J/cm². Ablation at a low fluence of 1 J/cm² eventually produces defined “cones” as the laser pulses progress from 10 to 100 pulses/site, and become more defined as the pulses reach 1000 pulses/site. The cones are directed toward...
the incident laser beam, and are the result of cumulative shadowing caused by ripples in the incomplete melt zone of the interaction site. Typically, the formation of cones is an indication of non-congruent evaporation. At 2 J/cm² the result was eventual partial cone and molten zone formation as 1000 pulses/site is achieved. At fluences of 3, 4, and 5 J/cm², a smooth melt zone is produced quickly, and produced increasing degrees of a re-

**Figure 3.6a.** SEM images of the UV KrF excimer only, laser-target interaction sites for fluences of 1, 2, and 3 J/cm², and cumulative laser pulses per site of 10, 100, and 1000.
solidified molten zone. It can be seen that 1000 pulses/site long order ripples or waves have started to form.

Figure 3.6b. SEM images of the UV KrF excimer only, laser-target interaction sites for fluences of 4 and 5 J/cm², and cumulative laser pulses per site of 10, 100, and 1000.
The effect of the cumulative laser ablation on the target composition was investigated by EDS after 1000 pulses for the different laser fluences. The results were normalized to germanium with an atomic percentage of 30% (Ge30), to be compared to the intrinsic Ba8Ga16Ge30 clathrate (Table 3.5). The results for the un-ablated target are given as reference. It can be seen that at low fluences, 1 and 2 J/cm², there is a significant deficiency of barium and slight excess gallium, relative to germanium and as compared to the original target and higher fluences. This is due to the incomplete melt of the target at low fluences, allowing the lower boiling point barium (2171 K) to be evaporated at a higher rate than the other components (Ga 2478 K, Ge 3107 K). Properties of the target components, barium, gallium, and germanium are listed in Appendix C. This non-uniformity in evaporation can cause non-congruent expansion in the ablated plume and/or non-stoichiometric deposition on the film.

The presence of the molten zone produced with higher laser fluences is more conducive for stoichiometric evaporation and this conclusion is supported by the energy dispersive spectroscopy (EDS) scans of the ablated spots on the target, which is presented

Table 3.5. Laser-target interaction site composition by EDS for excimer laser fluences 1 to 5 J/cm² after 1000 pulses. The intrinsic and un-ablated target values are listed also. The Ga/Ge ratio is calculated for each.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic %</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba</td>
<td>Ga</td>
<td>Ge</td>
<td>Ga/Ge</td>
</tr>
<tr>
<td>Intrinsic</td>
<td>8.0</td>
<td>16.0</td>
<td>30.0</td>
<td>0.533</td>
</tr>
<tr>
<td>Target</td>
<td>8.8 ± 0.4</td>
<td>15.8 ± 0.7</td>
<td>30.0 ± 0.9</td>
<td>0.53 ± 0.04</td>
</tr>
<tr>
<td>1 J/cm²</td>
<td>6.4 ± 0.4</td>
<td>17.5 ± 0.4</td>
<td>30.0 ± 0.7</td>
<td>0.58 ± 0.01</td>
</tr>
<tr>
<td>2 J/cm²</td>
<td>7.0 ± 0.2</td>
<td>16.6 ± 0.6</td>
<td>30.0 ± 0.6</td>
<td>0.55 ± 0.01</td>
</tr>
<tr>
<td>3 J/cm²</td>
<td>7.3 ± 0.2</td>
<td>16.1 ± 0.6</td>
<td>30.0 ± 0.7</td>
<td>0.54 ± 0.01</td>
</tr>
<tr>
<td>4 J/cm²</td>
<td>7.3 ± 0.2</td>
<td>16.1 ± 0.6</td>
<td>30.0 ± 0.8</td>
<td>0.54 ± 0.01</td>
</tr>
<tr>
<td>5 J/cm²</td>
<td>7.7 ± 0.5</td>
<td>16.0 ± 0.6</td>
<td>30.0 ± 0.7</td>
<td>0.53 ± 0.01</td>
</tr>
</tbody>
</table>
in Table 3.5. At a 1 J/cm² excimer laser fluence, as the ablation continues, the target had greater deficiency of the more volatile barium, signifying germanium enrichment.

### 3.4. Investigation of the CO₂ Laser - Target Interaction

The laser - target interaction was further studied by the CO₂ laser - target interaction and the single-beam transient reflectivity. The results presented here will be combined with the results of the excimer laser – target interaction investigation (Chapter 3.3) for the investigation of the dual-laser - target interaction.

Long wavelength, 10.6 μm, CO₂ laser pulses usually induce a “thermal” evaporation process [82], which can lead to non-congruent evaporation. Evaporation of the target material is not the goal of this investigation, whereas the purpose is to determine conditions to provide surface melting with minimal ablation. The SEM images (Figure 3.7) of the CO₂ laser-target interaction site for an un-ablated target, and at 1000 pulses each for fluences of 0.6, 1.3, 1.8, 2.0 and 2.4 J/cm², are shown in Figure 3.7. A fluence of 0.6 J/cm² produced slightly detectable melt of the smallest particles on the target surface, even after 1000 pulses. Increasing fluence through 2.4 J/cm² resulted in an increasingly partial melt of the target surface. The higher fluences produced a partial melt that re-solidified into larger feature than the original target granule sizes. The laser fluences from 0.6 to 1.8 J/cm² did not produce detectable plasma generation nor ablation of the target. The higher fluence of 2.4 J/cm² was observed to produce strong plume production and emission, which is undesirable for use during dual-laser ablation.

The effect on the target composition was investigated by EDS after 1000 pulses for the different IR laser fluences, as with the UV irradiation, shown in Table 3.6. It can
be seen that there is no significant change in the percentage of the elemental composition of the target. There is a slight non-significant increase in the barium content as the fluences increases, as compared to the bare target, possibly due to a higher absorption of far IR irradiation by the germanium.

The appropriate CO₂ laser energy to be utilized for dual-laser ablation is determined by the amount of surface melt and ablation. The surface morphology investigation allows for the observation of a cumulative effect. However, the effect is not conveyed as a temporal evolution. Temporal synchronization is determined by the on-set of the target surface melt measured by single-beam transient reflectivity observations.

The single-beam transient target reflectivity method [49] is used to obtain information about target surface modifications by observing the temporal profile of the

Figure 3.7. SEM images of the IR CO₂ laser only, laser-target interaction sites at 1000 pulses per site for fluences of 0.6 J/cm², 1.3 J/cm², 1.8 J/cm², 2.0 J/cm², and 2.4 J/cm².
reflected laser pulse as it interacts with the target. As the target melts, it become smoother and the surface is expected to result in the enhancement of the reflection, followed by a decrease due to absorption of the remainder of the pulse into the self-ablated plume. This single beam configuration provides a simple way of monitoring the plume cutoff so that the time for the melting ($\tau_m$) can be observed directly.

Figure 3.8 illustrates the CO$_2$ laser single-beam transient reflectivity configuration. The target surface was polished to aid in the detector alignment since the intensity of the reflected portion of the beam is significantly weaker than the monitor pulse. IR detector 1 was used to monitor the initial laser pulse shape directly, so that the scattered pulse collected by IR Detector 2 could be compared to the actual laser pulse directly for each individual laser pulse. Both of the detectors were high sensitivity HgCdTe infrared detectors to permit single shot detection for very weak probe levels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic %</th>
<th>Ga/Ge</th>
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<td>Ga</td>
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<td>16.0</td>
</tr>
<tr>
<td>Target</td>
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</tr>
<tr>
<td>1.3 J/cm$^2$</td>
<td>8.8±0.5</td>
<td>15.7±0.7</td>
</tr>
<tr>
<td>1.8 J/cm$^2$</td>
<td>8.8±0.2</td>
<td>15.7±0.6</td>
</tr>
<tr>
<td>2.0 J/cm$^2$</td>
<td>8.8±0.6</td>
<td>15.7±0.9</td>
</tr>
<tr>
<td>2.4 J/cm$^2$</td>
<td>9.1±0.1</td>
<td>16±0.9</td>
</tr>
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</table>

Table 3.6. Laser-target interaction site composition by EDS for CO$_2$ laser fluences 0.6 to 2.4 J/cm$^2$ after 1000 pulses. The intrinsic balanced and un-ablated target values are listed also. The Ga/Ge ratio is calculated for each.
Consistent with results of the CO\textsubscript{2} laser-target interaction investigation, a CO\textsubscript{2} laser fluence of 0.6 J/cm\textsuperscript{2} did not result in appreciable melting of the target surface. This fluence was then chosen for alignment and calibration of the single-beam transient measurements, which involves a degree of difficulty due to the low light level that reaches the reflection detector. The properly aligned and calibrated monitor and reflection pulses (Figure 3.9) will over-lap one another well with proper alignment, with only a

Figure 3.8. The schematic diagram of the experiment setup for the single-beam transient target reflectivity measurements.
Figure 3.9. The monitor pulse before target interaction and reflection pulse after target interaction. The 0.6 J/cm² CO₂ laser fluence was used for alignment and calibration.

Figure 3.10. Representation of IR reflection pulse showing features: on-set of melt, on-set of ablation, and peak of the monitor pulse.
reduced change in magnitude for the reflected pulse. Figure 3.10 schematically demonstrates the features of the reflected pulse that are noted; (i) on-set of the target surface melt ($\tau_m$), (ii) onset of ablation/evaporation of the molten material, in reference to (iii) the peak of the monitor pulse.

The target was impinged by CO$_2$ laser pulses of 1.8, 2.0, and 2.4 J/cm$^2$ and the reflection pulses were recorded concurrently with the monitor pulse (Figure 3.11a-c) respectively. Each recorded pulse is for a single pulse per target location. Each subsequent pulse was on an un-ablated region of the target as to not record a cumulative effect. The results of 1.8 J/cm$^2$ (Figure 3.11a) show a late arrival and low onset of melt increase 115 ns before the peak, with little to no ablation contribution. The late onset of melt may not allow sufficient CO$_2$ laser energy remaining to interact with the excimer laser generated plasma. The 2.0 J/cm$^2$ fluence (Figure 3.11b) had a 145 ns time span before the pulse peak and weak ablation. The 2.4 J/cm$^2$ fluence (Figure 3.11c) had a 180 ns time difference, causing melting at the onset of the pulse and significant ablation, not desired in this process. The transient reflectivity results combined with the surface morphology and compositional results lead to 2.0 J/cm$^2$ CO$_2$ laser fluence being the most promising candidate for use with dual-laser ablation. When the excimer laser pulse is synchronized with the CO$_2$ laser pulse during dual-laser ablation, based on the above results the on-set of the excimer laser pulse should occur at the same time as the on-set of the melt ($\tau_m$).
Figure 3.11. Single-beam reflectivity for CO$_2$ laser fluences of (a) 1.8 J/cm$^2$, (b) 2.0 J/cm$^2$, and (c) 2.4 J/cm$^2$, before (Monitor) and after Reflection from the Ba$_3$Ga$_{16}$Ge$_{30}$ target, displaying on-set of melt.
3.5. Investigation of the Dual-Laser - Target Interaction

Based upon the results of the investigation of excimer laser-target interaction (Section 3) and the investigation of CO₂ laser-target interaction (Section 3.4), moderate laser fluences were combined for the dual-laser ablation technique. The low excimer laser fluence of 1 J/cm² was chosen as the excimer laser energy density. This investigation is to determine if the cumulative surface features and non-congruent evaporation can be controlled when coupled with the appropriate CO₂ laser energy. Referring to Section 3.3 Figure 3.6a, after 10 laser pulses with 1 J/cm², the laser-target interaction site had a smooth melt zone. The goal is to maintain this when coupled with the CO₂ laser pulse. The results of the CO₂ laser-target interaction and single-beam transient reflectivity studies lead to the selection of 2.0 J/cm² CO₂ laser fluence, and an excimer laser pulse on-set of approximately 60-80 ns (100-120 ns p-p delay) (Figure 3.12).

![Figure 3.12](image-url)  
**Figure 3.12.** The monitor oscilloscope traces of the UV excimer laser pulse and the IR CO₂ laser pulse with a 100-110 ns p-p delay. The on-set of the melt is indicated at \( t_m \).
SEM images of the dual laser-target interaction sites for 10, 100, and 1000 pulses/site for laser fluences of 1 J/cm² UV coupled with 2 J/cm² IR and a 100-110 ns p-p delay are shown in Figure 3.13. These parameters produced and maintained a smooth melt zone through all laser pulse/site conditions. This is similar to the high fluence single-laser ablation results, but without the long order surface waves (see Figure 3.6a and b). These dual laser-target surface modification results are conducive for reduced particulate generation.

Figure 3.13. Images of the laser-target interaction sites for 10, 100, and 1000 pulses/site using dual-laser fluences of 1 J/cm² UV and 2 J/cm² IR with 100 - 110 ns p-p delay.

It was observed that proper evaporation using the dual-laser technique with these parameters is dependent on the target surface preparation. Polishing the target surface prior to ablation controlled the formation of conical features on the surface. The dual-laser ablation was able to maintain a smooth melt feature when starting from a smooth target, but could not produce a smooth melt from a target surface that began with an unpolished, granulated target surface (Figure 3.14). Rastering the laser spot location across the rotating target during long deposition runs can be used to also minimize feature formation. Spot rastering was performed to minimize the average laser pulses per site to
have a quantity of pulses/site which was comparable to other single-laser fluences during film deposition investigations.

Figure 3.14. SEM images of dual-laser ablation of an unpolished target. A region of un-ablated target surface is shown and the laser-target interaction sites for 10, 100, and 1000 pulses/site using dual-laser fluences of 1 J/cm² UV and 2 J/cm² IR with 100 ns p-p delay.

The effect on the target composition was investigated by EDS after 1000 pulses per site for the different laser fluences, as shown in Table 3.7. The dual-laser results are shown compared to the excimer-only laser fluence of 1 J/cm². The dual-laser was also compared to the excimer-only single-laser fluence of 3 J/cm² since the melt zones had a similar appearance. The results were normalized to germanium with an atomic percentage of 30% (Ge₃₀), to be standardized to the Ba₈Ga₁₆Ge₃₀ clathrate. The result for the un-ablated target was not irradiated by the pulsed laser. The dual-laser ablation resulted in
near-stoichiometric evaporation and a significant improvement as compared to the excimer-only laser fluence of 1 J/cm².

Table 3.7. The actual composition and Ga/Ge ratio of the un-ablated target and laser-target interaction sites after 1000 pulses per site for dual-laser 1 J/cm² UV coupled with 2 J/cm² IR with 100 – 110 ns p-p delay. The results for excimer-only single-laser 3 J/cm² (S₃) and 1 J/cm² (S₁) are included for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic %</th>
<th></th>
<th></th>
<th>Ga/Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba</td>
<td>Ga</td>
<td>Ge</td>
<td></td>
</tr>
<tr>
<td>Balanced</td>
<td>8.0</td>
<td>16.0</td>
<td>30.0</td>
<td>0.533</td>
</tr>
<tr>
<td>Target</td>
<td>8.6±0.4</td>
<td>15.6±0.2</td>
<td>30.0±0.2</td>
<td>0.52±0.01</td>
</tr>
<tr>
<td>Dual</td>
<td>7.6±0.1</td>
<td>15.7±0.2</td>
<td>30.0±0.1</td>
<td>0.52±0.01</td>
</tr>
<tr>
<td>S₃</td>
<td>7.3±0.1</td>
<td>15.9±0.5</td>
<td>30.0±0.7</td>
<td>0.53±0.01</td>
</tr>
<tr>
<td>S₁</td>
<td>6.5±0.4</td>
<td>17.6±0.7</td>
<td>30.0±0.9</td>
<td>0.59±0.03</td>
</tr>
</tbody>
</table>

3.6. Summary

Based upon general qualities of type-I clathrate Ba₈Ga₁₆Ge₃₀, high quality thin-film deposition by PLD may incur some challenges. These qualities include the complex clathrate crystal structure, multi-component material with widely varied physical properties, and cold-pressed powder target as the source. Investigation of the target surface modification by pulsed laser ablation was undertaken to gain understanding of the parameters that can be controlled to provide ablation conditions that may be conducive for quality thin film deposition.

The target surface irradiation using KrF excimer-only single-laser ablation revealed that use of low fluences produced conical surface modifications and non-congruent evaporation of the material. High fluence ablation produced near congruent
evaporation with smooth laser-target melt zone, which is conducive for good film deposition. However, fluences greater than 3 J/cm² do not appear to result in an increased benefit. The laser-target interaction was also investigated using the dual-laser ablation technique. Based on the excimer-only investigations and CO₂ laser-only results, it was found that conducive evaporation conditions could be achieved using low to moderate laser fluences. Coupling 2 J/cm² CO₂ laser fluence with the 1 J/cm² excimer laser generated plasma produced results comparable to those of high fluence excimer-only results.

The outcome of this surface modification investigation have provided the ablation conditions that can now be used during in-situ optical emission studies of the laser generated plasma. Optical diagnostic studies can further the understanding of the evaporation processes that occur during pulsed laser ablation of this particular material.
CHAPTER 4:
IN-SITU OPTICAL DIAGNOSTICS

During the laser-target interaction in pulsed laser ablation the evaporated material forms a plasma whose ion density is determined by the laser parameters. The plasma contains both multiply ionized species and highly excited species. Subsequent expansion of the plasma and collisional excitation of the ionized and excited species extend the visible emission in a plume of material traveling from the target to the substrate. In-situ optical diagnostics provides a non-invasive probe to investigate atoms, ions, and molecules within the laser-generated plasma without interfering with the ablation process. It can yield information about properties such as excited state species densities, collisional effects, and distribution of species to name a few. These details are utilized to develop a physical understanding about the plasma dynamics that affect the growth of stoichiometric Ba$_8$Ga$_{16}$Ge$_{30}$ films.

A number of diagnostic techniques have been developed to assist in the characterization of plume dynamics, such as spectroscopic analysis and time-gated imaging. Optical emission spectroscopy (OES) is well suited to yield information about PLD ablation plumes. Emission spectroscopy is used to identify the species in the laser ablated plume from referenced atomic lines [83]. The emission intensity is very high during the initial stages of plume expansion corresponding to a continuum of radiation through the visible spectrum. The plasma appears white within the first millimeter of
expansion. After expansion to distances of a few millimeters, PLD plumes exhibit an assortment of atomic and ionic lines. The spectral intensities change dramatically with time as the atoms cool and de-excite.

Imaging techniques are extremely useful for studies of ablation plumes in vacuum by providing two-dimensional snapshots of the three-dimensional plume propagation and dynamics. This capability becomes essential for understanding of the plume propagation. Intensified charge coupled device array (ICCD) cameras allow high-speed photography with the use of electronic gates that can be used to dynamically image the plume emission [84, 83]. The light emitted by the excited sample can be spectrally resolved through the use of notch filters to yield qualitative and quantitative information on the elemental constituents of the sample.

In a typical optical emission diagnostics system the plasma plume is imaged outside of the vacuum chamber using relevant optical elements (Figure 4.1). A specific object plane along the axis of the plume is imaged onto a plane which is incident to optical fibers or directly onto the detector of the camera. This arrangement allows collection of light from a specific position, a plane or points on that plane, within the plasma while contributions from other positions are minimized, as shown in Figure 4.1.

Optical plasma emission measurements may be time-gated dependent upon the information desired. Time-integrated data collection from the entire laser generated plume volume is adequate for species identification or expansion profiles. This involves gating on the order of micro-seconds or longer. However, spatially and temporally resolved measurements are necessary to infer the time-of-flight (TOF) and local populations. Time-resolved measurements require gating on the order of nano-seconds.
Key parameters for determining the quality of a growing film are the kinetic energy of the species and the stoichiometry of the components [85]. Optical determination of the time-of-flight (TOF), and in turn the velocity, is an attractive method for estimating the energy of the species [86]. Insight into stoichiometric deposition is examined by comparative species expansion profiles. The OES and ICCD imaging techniques were utilized for characterization of the pulsed laser generated plasma.

4.1. Experimental Details

The experimental set-up consists of the dual-laser ablation system described in Chapter 2.3 with the integration of the optical diagnostics system (Figure 4.2a-b). The center piece of the in-situ optical diagnostics is the high speed ICCD camera. The ICCD
Figure 4.2. The schematic diagrams of the dual-laser deposition system with the (a) optical emission spectroscopy (OES), and (b) intensified charge-coupled device (ICCD) imaging system included.
camera was interchangeable between the two configurations, OES (Figure 4.2a) and ICCD imaging (Figure 4.2b). The camera was part of a PI Acton PI-MAX:512 UNIGEN Digital ICCD Camera System, with $512 \times 512$ pixels ($19 \times 19$ µm pixel active area), $12.4 \times 12.4$ mm image area, and < 5 ns gating capable (see Appendix D). The gating capability allows for high speed, short time frame exposure to be used for laser generated plume analysis. The spectral sensitivity of the camera ranges from 150 nm (UV) to 925 nm (Figure 4.3). The timing of the camera is controllable by the Programmable Timing Generator (PTG).

![Figure 4.3](image_url)

**Figure 4.3.** Specification of the wavelength sensitivity of the ICCD camera. The wavelength cut-off due to the imaging window is shown at 350 nm.

The spectrometer (Appendix E) used in the OES experiments, was a 500 mm focal length, Czerny-Turner type, with 1:1 magnification, and triple indexable gratings (150, 600, and 1200 grooves/mm), adjustable entrance slit set to 10 µm, and resolution to
0.05 nm. The optical fiber bundle (Appendix F) was a three fiber bundle with 200 µm diameter fibers (~245 µm dia. with cladding). The spectrometer was joined with the ICCD camera to produce broad range wavelength spectrums of the emission, as in an optical multi-channel analyzer (OMA) system, also referred to as time-integrate space-resolved laser-induced plasma spectroscopy (TISR-LIPS) [87].

The camera, spectrometer, and PTG were controlled by the WinSpec/WinView software (version 2.5.21.0,). The software is for real-time acquisition, display, and data processing operated under Microsoft Windows 2000/XP. The OES and ICCD imaging standard operating procedure for data collection and analysis is given in Appendix G.

The imaging system was a 10.5 cm focal length lens set, which was positioned perpendicular to the plume axis. The optic axis of the lens system was centered 2 cm from the face of the target, see Figure 4.1. The axis of the luminous laser-generated plume (object) was imaged onto a plane outside the deposition chamber. A magnification of \(-\frac{1}{2}\) was produced for use during OES. The fiber was able to be translated in the \(x-y\) plane of the image plane. During ICCD imaging, the lens position was adjusted to produce a -1/4 magnification and the camera was positioned so that the image plane formed on the front surface of the camera’s ICCD detector. The camera was mounted on a stage with \(y-z\) axis adjustment to facilitate proper focus of the image and positioning of the image on the detector of the camera. The entire target-substrate distance of 4 cm was detectable without requiring movement of the camera.

The system is aligned and calibrated by placing a standard source (helium lamp) on-axis in place of the target and substrate. The lamp was masked to simulate the 4 cm target-substrate distance. This alignment was performed to minimize effects due to
distortion and aberration caused by the optical elements of the system such as windows, lenses, filters, and fiber optics. The position of the lens was adjusted to minimize image distortion losses, and position of the optical fiber or camera detector was defined relative to the aligned image plane. Figure 4.4a shows an example of the properly aligned image system and Figure 4.4b is an example of the distortion that can result due to misalignment. The He lamp was translated vertically along the object plane (Figure 4.5) and He spectrums were recorded by OES at various x-y positions. The optical fiber position was translated horizontally (0 to 40 mm) and also vertically (-30 mm to 30 mm) as the lamp was moved. The normalized intensity of the 587.6 nm wavelength line of He, as a function of the x-y plane position of the optical fiber is shown in Figure 4.6. This gives a representation of the field of view of the imaging system without resulting in losses due to distortion. The alignment allows quality image rendition within the needed
0 – 40 cm horizontal range from -20 to 20 cm vertically. The spectrometer and data collection software were also calibrated in this fashion to account for contributions due to the optical system components. The image magnification and orientation were determined by placing a scale card between the target and substrate holder (Figure 4.7). The scale card is aligned along the plume axis then back-lit and focused onto the image.

**Figure 4.5.** Schematic diagram of the imaging system alignment and calibration layout using a helium lamp masked for 4 cm length. The diagram is drawn to scale.
Figure 4.6. Intensity of the He lamp (587.6 nm wavelength) as the optical fiber position was varied along the $x$-axis (horizontal) and $y$-axis (vertical) of the image plane.

Figure 4.7. The (a) back-lit scale card used to determine image magnification and orientation for the optical diagnostics system(s), and (b) a photograph of the imaged card.
plane. The timing of the in-situ optical diagnostics system was triggered ($t_0$) simultaneously with the excimer laser via the digital delay generator. The camera delay and gate-width were controlled by the $t_0$ triggered PTG.

4.2. ICCD Imaging

4.2.1. Dual-Laser Synchronization by In-Situ Optical Diagnostics

The laser generated plume emission and expansion is observed to increase dramatically when the excimer laser generated plasma is efficiently coupled with the CO$_2$ laser energy. When the synchronization is optimized for given laser parameters the plume ionization, plume expansion, and particle reduction are enhanced [48, 69]. The proper temporal synchronization of the dual-laser inter-pulse delay can be determined by the maximum expansion and emission of the plume when optimum energy coupling has occurred.

To illustrate the CO$_2$ laser-only interaction with the target, time-integrated ICCD images of laser ablation at various CO$_2$ laser fluences were recorded (Figure 4.8). A fluence of 1.8 J/cm$^2$ (Figure 4.8a) results in visible thermionic emission; however there is no visible emission from a plasma or plume formation. 2.0 J/cm$^2$ (Figure 4.8b) created weak visible plume emission, while 2.4 J/cm$^2$ (Figure 4.8c) produced strong plasma and plume formation. The dramatic increase in the ablation with the 2.4 J/cm$^2$ as compared to the lower fluences is shown in Figure 4.9 by time-resolved emission imaged at the target surface. These results support the on-set of the melt studies by single-beam transient reflectivity in Chapter 3 Section 4. Although the CO$_2$ laser fluence of 2.4 J/cm$^2$ independently produces strong ablation and emission, but when coupled with the excimer
laser generated plasma it would result in excessive target surface temperatures causing increasing evaporation and particulate production and would be counter-productive.

The ICCD imaging configuration, Figure 4.2b, of the in-situ optical diagnostics system was utilized for the following results, as well as the object plane of the plume

![Figure 4.8](image.png)

**Figure 4.8.** Time-integrated ICCD images of CO₂ laser-target interactions with laser fluences of (a) 1.8 J/cm², (b) 2.0 J/cm², and (c) 2.4 J/cm². Images are normalized with respect to image (c).

![Figure 4.9](image.png)

**Figure 4.9.** The normalized time-resolved total emission intensity of the CO₂ laser-target interactions for 1.8 J/cm², 2.0 J/cm², and 2.4 J/cm². The emission was imaged at the target surface (0 mm position).
described in Figure 4.1. The length of the viewable area imaged in Figure 4.10 is approximately 48 mm. The following results presented in this section utilized time-integrated gating to capture all the light emitted during the ablation process.

![ICCD imaging of total emission of ablated plumes from the target for (a) 1 J/cm² and (b) dual-laser ablation.](image)

**Figure 4.10.** ICCD imaging of total emission of ablated plumes from the target for (a) 1 J/cm² and (b) dual-laser ablation.

The total intensity of the plume emission was recorded for the single-laser low fluence of 1 J/cm² and again when coupled with the addition of the 2 J/cm² IR CO₂ laser pulse at various peak-to-peak (p-p) delays. Examples of single-laser and dual-laser generated plasmas are shown in Figure 4.10a and b, respectively. Also, examples of the in-situ monitored laser pulse delays for -25 ns, 100 ns, and 175 ns p-p delays are shown in Figure 4.11. The ICCD camera system was synchronized to the triggering of the excimer laser and recorded each event for 20 µs to ensure that the entire plume emission was captured (time-integrated). The p-p delay was varied from -50 ns to 200 ns, relative
to the peak of the excimer laser pulse at 0 ns. The on-axis intensity (Figure 4.12.a), and cross-sectional FWHM (Figure 4.12.b) of the plume was measured 250 µm from the target surface. This observation position is beyond the edge of the laser induced plasma, within the 2 × 3 mm laser spot size, and before significant plume expansion and ion recombination has occurred. The cross-sectional expansion profiles were compared (Figure 4.12) and the on-axis intensity of the dual-laser induced plume was observed to minimize as the FWHM maximized. Maximum plume expansion is indicative of optimum energy coupling of the CO2 laser pulse into the excimer laser pulse generated plasma as the plume becomes less forward-directed and broader expansion occurs due to the higher temperatures of the plasma which can result in greater species ionization [48].

The minimum on-axis intensity occurred when the $p-p$ inter-pulse delay was between 105-125 ns, and the maximum cross-sectional FWHM occurred between 80-105 ns. It is

![Figure 4.11. Overlapped oscilloscope traces for the excimer laser pulse (UV) and CO2 laser pulses (IR) for peak-to-peak delays of -25 ns, +100 ns, and +175 ns, relative to the UV pulse at 0 ns.](image-url)
evident from Figure 4.10b, with the 100 ns delay, that the plume expansion is dramatically greater for the dual-laser emission as compared to the excimer-only single-laser expansion.

![Figure 4.12](image-url)

**Figure 4.12.** Dual-laser synchronization parameters as a function of the dual-laser pulse peak-to-peak delays obtained by total emission ICCD imaging of the laser induced plasma expansion. The (a) normalized peak intensity and (b) normalized FWHM are shown.
4.2.2. Elemental Expansion Profiles

To investigate the expansion and species ionization, the laser generated plumes were imaged with the addition of notch filtering. Wavelength filters were individually placed in the optical path before the detector of the ICCD camera. The optical filters were chosen based on NIST emission spectra tables as strong lines and not overlapping or near other emission lines. The filters for singly ionized barium (Ba$^+$ 455 nm), gallium (Ga$^+$ 426 nm), and germanium (Ge$^+$ 481 nm) were implemented in this study. The ICCD images of the laser generated plumes for single-laser ablation low fluence (1 J/cm$^2$ UV), single-laser ablation high fluence (3 J/cm$^2$ UV), and dual-laser ablation (1 J/cm$^2$ UV + 2 J/cm$^2$ IR), respectively, are shown in Figure 4.13. The results displayed also include unfiltered emission (total emission of the plume), allowing the contribution from the entire detectable spectrum to be recorded (350 nm – 925 nm). The pseudo-color intensity of the images is normalized relative to each other.

The emission from the excimer-only low fluence configuration was very weak for all three element wavelengths, as compared to the single-laser high fluence and dual-laser ablation results. It results from coupling the CO$_2$ laser energy into the low fluence excimer laser generated plasma can be clearly seen. The emission is greatly increased, as is the expansion. As a comparison, the dual-laser expansion is significantly greater than the high fluence single laser ablation.

The angular distribution of the OES cross-section of ablated plumes 5 mm from the target was derived from the wavelength filtered images (Figure 4.14). To compare all three laser configurations, the 5 mm on-axis distance was chosen because beyond this distance the emission from the low fluence single–laser ablation was depleted below
detectable values for the parameters utilized here. The emission shown is for \( \text{Ba}^+ \) 455 nm, \( \text{Ga}^+ \) 426 nm and \( \text{Ge}^+ \) 481 nm. The species dependent intensity profiles for (a) 1 J/cm\(^2\) and (b) 3 J/cm\(^2\) single-laser, and (c) dual-laser ablation, are shown in Figure 4.14a-c. The results of the full width at half maximum (FWHM) of the OES profiles are summarized

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**Figure 4.13.** ICCD imaging of the time-integrated laser generated plume emission for excimer only 1 J/cm\(^2\) (S1), high fluence single-laser 3 J/cm\(^2\) (S3), and dual-laser ablation. For each laser configuration the unfiltered total emission, \( \text{Ba}^+ \) 455 nm, \( \text{Ga}^+ \) 426 nm, and \( \text{Ge}^+ \) 481 nm are shown.
Figure 4.14. OES cross-section of ablated plumes 5 mm from the target for (a) 1 J/cm² and (b) 3 J/cm² single-laser, and (c) dual-laser ablation. The emission shown is for Ba⁺ 455 nm, Ga⁺ 426 nm and Ge⁺ 481 nm.
in Table 4.1. The expansion for the dual-laser ablation generated plume is significantly broader and more congruent, as compared to either single-laser configuration. The average FWHM expansion of the dual-laser ablated plume is 1.7 to 3.1 times greater than the single-laser plumes.

**Table 4.1.** The full width at half maximum (FWHM) of the OES cross-section profile of ablated plumes 5 mm from the target for (a) 1 J/cm² and (b) 3 J/cm² single-laser, and (c) dual-laser ablation. (± 1.5 degree)

<table>
<thead>
<tr>
<th></th>
<th>FWHM (deg)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Ba</td>
</tr>
<tr>
<td>S₁</td>
<td>29.4</td>
</tr>
<tr>
<td>S₃</td>
<td>33.4</td>
</tr>
<tr>
<td>Dₐ</td>
<td>67.4</td>
</tr>
</tbody>
</table>

The optical emission from the Ba₈Ga₁₆Ge₃₀ plume demonstrates that the coupling of the CO₂ laser into the excimer laser-generated plume causes both significant ionic excitation in addition to lateral plume expansion, as previously demonstrated with other materials [48, 68]. The highly ionized material and congruent expansion profiles of the dual-laser process are desirable for quality film depositions, leading to stoichiometric deposition of the material. Congruent evaporation is one of the important advantages of pulsed laser evaporation (pulse widths < 1 µs) for deposition of multi-component materials [53]. There are exceptions, however, where evaporation is incongruent even under pulsed laser heating [90, 91], such as a volatile element component of the compound causing preferential evaporation leading to non-stoichiometric depositions. The lower boiling point of the barium has been found to be problematic for a laser energy density (1 J/cm²) near the excimer laser ablation threshold for Ba₈Ga₁₆Ge₃₀, however, this is circumvented with the utilization of dual-laser ablation.
4.3. Optical Emission Spectroscopy

OES is primarily used for identification of the species in the laser generated plume from tabulated atomic lines and molecular bands [84]. Time-integrated spectra from the entire plume volume are adequate for this task. However, spatially and temporally resolved measurements are necessary to infer the time-of-flight (TOF) and local populations. After expansion to distances of a few millimeters, PLD plumes generally exhibit a rich assortment of atomic and ionic lines. Because the interpretation of OES observations is dependent on the source of emission and the understanding of the physical processes occurring within the source, care must be taken in the interpretation of these observations [92].

The laser-generated plume was characterized by viewing the optical emission of the plume perpendicular to the axis of propagation (Figure 4.1). The spectra of the plume were obtained using the OES configuration of the in-situ optical diagnostics system, Figure 4.2a. The optical fiber was positioned to collect light which was imaged 2 cm away from the target surface, along the plume/optic axis. The spectrum was started at 400 nm due to the complete transmission cut-off at 350 nm from the deposition chamber imaging window (Borofloat). The time-integrated spectra were collected for the excimer only portion (1 J/cm²), and dual-laser 100 ns p-p delay (1 J/cm² UV + 2 J/cm² IR) ablation, Figures 4.15a and b, respectively. The spectra have shown on the same scale for comparison and show the relative emission of the excited species. The neutral (I) and singly (II) ionized elements are identified for barium, gallium, and germanium [93]. The increased singly ionized intensities of the dual-laser configuration can be clearly seen, demonstrating the effect of coupling the energy of the CO₂ laser pulse with the excimer
laser generated plasma. Under the optimum conditions, highly excited and ionized plumes can be produced while using moderate laser fluences. The higher ionization leads
to generation of energetic species and their impingement on the film growth surface plays an important role in the nucleation structure of high quality thin-film growth [53].

While ablating the rotating target with low excimer laser fluence, it was observed that the optical emission intensity decreased as the total laser pulses accumulated. The time-integrated intensity for the visible spectrum (400 nm to 715 nm) was recorded on-axis, 2 cm from the target, as a function of cumulative laser pulses. The normalized intensity for single and dual-laser PLD is shown in Figure 4.16. As the laser pulses accumulate, the intensity decreases for the single-laser PLD process but remains constant for the dual-laser PLD. This effect may be due to the changing target surface topography from the impinging excimer laser pulses for low fluence ablation, as seen in Chapter 2, causing reduced absorption of the laser energy into the target surface. As for the dual-laser process, the target surface topography is smoother as a result of the more complete melt zone, providing a more consistent plume as the ablation of the target progresses.

![Graph showing normalized intensity versus pulses for single and dual-laser ablation.](image)

**Figure 4.16.** The total intensity of the time-integrated optical emission obtained 2 cm from the target surface for cumulative laser pulse for single and dual-laser ablation.
Spatially and temporally resolved measurements were utilized to measure time-of-flight (TOF) of the transient plume for determination of the velocity of the ablated material. This velocity is proportional to the kinetic energy of the emitting material. The emission temporal profiles were recorded for the laser-generated transient plumes for 1 J/cm² and 3 J/cm² excimer single-laser ablation and dual-laser ablation. The optical fiber was translated along the optical axis of the image plane a distances of 0 mm, 1 mm, 2 mm, 4 mm, and 6 mm, for each laser condition. The peak of the 0 mm position TOF data is utilized as a reference point to calibrate the distance and time \(t_0\) equal to zero. The smallest feasible camera time-gate was used for each condition in order to measure the emission for only a small increment of time at a given distance from the target, while still being able to measure appropriate emission intensity. This will aid increasing the signal-to-noise ratio at larger distances from the target and lower ablation energies. Due to the low intensity emission of the low fluence single-laser ablation, time-gates of 10 ns (at 0 mm) to 250 ns (at 6 mm) were required. The high fluence single-laser was gated at 10 ns each, while the dual-laser was gated at 20 ns each. At each position, the delay of the time-gate is increased from 0 to 1.5 \(\mu\)s in steps equal to the gate-width, in order to record the complete time evolution of the population passing that particular point.

An example of a time-gated TOF profile for a plume pulse arriving at a point 2 mm on-axis from the target surface with a 10 ns gate is shown in Figure 4.17. The peak of the intensity profile corresponds to the bulk of the light emitting material passing the imaged position. In the given example the peak on material passes the 2 mm point of interest, approximately 235 ns after the arrival of the laser pulse. This data is used to determine the velocity of the bulk of material and is referred as the TOF. The TOF
profiles for the three laser configurations (Figure 4.18a-c) are intensity normalized for each individual profile. The low fluence single laser TOF profiles (Figure 4.18a) occur later in time and are significantly broader than the profiles for high fluence single-laser and the dual-laser, Figure 4.18b and 4.18c, respectively. The time at which the peak intensity occurs is used to determine the TOF of the emitting material. The distance as a function of the peak time was plotted (Figure 4.19) and the slope was used to determine the velocity of the emitted material for each laser configuration. The material accelerates quickly in the initial stages of the plasma to a constant velocity. The low fluence single-laser ablation resulted in the lowest velocity, 0.63 cm/µs, and the broadest temporal FWHM (Figure 4.20). The high fluence single-laser and dual-laser ablation resulted in higher velocities, 0.90 and 1.56 cm/µs, respectively. However, the temporal FWHM for these two conditions were equal.

Figure 4.17. An example of a time-of-flight (TOF) profile positioned at 2 mm from the target surface.
Figure 4.18. The normalized intensity, time-resolved, total emission time-of-flight profiles for positions 0 mm, 1 mm, 2 mm, 4 mm, and 6 mm from the target surface. The profiles were imaged along the plume axis for single-laser (a) 1 J/cm², and (b) 3 J/cm² and (c) dual-laser ablation configurations. The dual-laser $p$-$p$ delay was 100 ns.
**Figure 4.19.** The distance-time plot of the TOF peak arrival time at various distances from the target surface, for single-laser 1 J/cm² and 3 J/cm², and dual-laser 1 J/cm² UV + 2 J/cm² IR. The slopes were velocity determination.

**Figure 4.20.** The temporal FWHM of the TOF profiles for single-laser 1 J/cm² and 3 J/cm², and for the dual-laser 1 J/cm² UV + 2 J/cm² IR.
The velocities of the individual elements were investigated to determine the difference between the velocities of the different species. Due to the low emission of Ga and Ge, relative to that of Ba, these velocities could not be resolved with certain accuracy (Figure 4.21). This has been observed elsewhere with other materials using laser ablation in vacuum, where individual species velocities have been found to not to be as expected [86].

![Normalized Intensity vs Time](image_url)

**Figure 4.21.** The time-resolved elemental TOF profiles for the ions Ba\(^+\) 455 nm, Ga\(^+\) 426 nm, and Ge\(^+\) 481 nm at 4 mm from the target surface.

### 4.4. Summary

Through the use of in-situ optical diagnostic techniques the time-gated and time-integrated plasma emission was investigated as a technique to facilitate the synchronization of the two lasers for dual-laser ablation. The optimum temporal \(p-p\)
delay was able to be determined for the coupling of the 1 J/cm² excimer laser-generated plasma with the 2 J/cm² CO₂ laser energy. Similar results were obtained when investigated by the laser-target interaction; however, the use of optical diagnostic techniques is a desirable in-situ process.

Results of the optical emission studies, thought the use of both ICCD imaging and OES, yielded insight into the nature of the ablated target material. The plasma expansion profiles found that the dual-laser technique produced broader and congruent expansion of the species which is conducive to improved film distribution and stoichiometric deposition. The OES studies demonstrated the higher species ionization and TOF also for the dual-laser technique. This is advantageous for producing high quality films with good adhesion and crystal structure.
CHAPTER 5:
HYDRODYNAMIC MODELING OF PLASMA EXPANSION

Results of hydrodynamic modeling of the laser-generated plasma expansion due to single-laser and dual-laser ablation of the Ba$_8$Ga$_{16}$Ge$_{30}$ target were evaluated. The interaction of the high-power laser pulses with bulk targets results in evaporation, plasma formation, and deposition of films. The mechanisms involved in the plasma expansion process were investigated by utilizing a theoretical model developed by Singh et al. [94] for simulating laser-plasma-solid interactions.

The model is based on gas dynamic equations where the laser-generated plasma is treated as an ideal gas at high pressure and temperature. This plasma volume is initially confined to the small dimensions of the laser spot size and plasma thickness, and then is suddenly allowed to expand in vacuum. The process can be classified into three regimes (Figure 5.1) [95]: (i) interaction of the laser beam with the bulk material resulting in evaporation of the surface layers (evaporation regime), (ii) interaction of the laser beam with the evaporated material leading to formation of a high-temperature isothermal expanding plasma consisting of positively charged and neutral particles, molecules, and atoms (isothermal regime), and (iii) the anisotropic three-dimensional adiabatic expansion of the laser-generated plasma and deposition of films (adiabatic regime). The first two regimes occur during the laser pulse duration ($t \leq \tau$), while the last initiates after the laser pulse terminates ($t > \tau$). The evaporation of the target is assumed to be thermal
in nature under pulsed laser evaporation conditions, while the plasma expansion dynamics is non-thermal as a result of interactions of the laser beam with the evaporated material. The gas dynamic equations simulate the expansion of the plasma in the last two regimes. The solution of the equations shows the expansion velocities of the plasma are related to its initial dimensions and temperature, and the atomic weight of the species.

The model has been shown to predict characteristic features of pulse laser evaporation and deposition of films [95]. The characteristics include (a) the pulse energy density effect on atomic velocities, (b) the forward-directed nature of the plasma and its dependence on energy density, (c) spatial compositional variations in multi-component thin films as a function of energy density, (d) dependence of the atomic velocities with atomic weights, (e) velocity distribution of the atomic and molecular species, and (f) thickness and compositional variations as a function of substrate-target distance and irradiated spot size.

Figure 5.1. Schematic diagrams showing the three regimes during the pulsed laser irradiation of a bulk target: the (a) evaporation regime \(0 < t < 100 \text{ps}\), (b) isothermal regime \((100 \text{ps} < t \leq \tau)\), and (c) the adiabatic regime \(t > \tau\).
The model was initially developed for simulation of single excimer-laser evaporation [94] but was modified for the dual-laser ablation technique [68]. The modified plasma model has been successfully used to simulate the film thickness profiles, plasma thickness [97], and species expansion profiles of multi-component materials [98] for single-laser and dual-laser techniques. Under dual-laser ablation, the addition of the synchronized, but longer pulse duration, CO$_2$ laser required the consideration of another isothermal regime during the initial stages of the plasma generation. For the results presented here, plasma model was applied to the time-of-flight (TOF) profiles of the single and dual-laser ablated plasmas presented in Chapter 4. The model was fitted to the experimental data through computation determination of plasma expansion parameters such as initial plasma thickness, temperature, and the expansion velocities.

5.1. Isothermal and Adiabatic Expansion Model

The rapid expansion of the laser-generated plasma in vacuum results from large density gradients. The plasma which is absorbing the laser energy can be simulated as a high-temperature high-pressure gas. In the initial stages of the plasma expansion the particle density is on the order of $10^{19}$-$10^{20}$ cm$^{-3}$, so the mean free path of the particles is short and the plasma behaves as a fluid. The equations of gas dynamics can be applied to simulate its expansion. In the theoretical model, the density and pressure profiles of the plasma are assumed to show an exponential decrease with distance from the target surface. The density ($n$) of the plasma at any given point $(x,y,z)$ at time $t$ can be expressed by [94];
\[ n(x, y, z, t) = \left( \frac{t}{\tau} \right) \left[ \frac{n_o}{X(t)Y(t)Z(t)} \right] e^{\left( \frac{-x^2}{2X(t)^2} - \frac{y^2}{2Y(t)^2} - \frac{z^2}{2Z(t)^2} \right)} \] (5.1)

Where \( n_o \) is the total number of evaporated particles at the end of the laser pulse \((t = \tau)\).

The pressure \((P)\) at any point in the plasma is related to its density by the ideal gas equation \((PV = nk_BT_o)\) and can be expressed by [94];

\[ P(x, y, z, t) = \left( \frac{t}{\tau} \right) \left( \frac{n_oT_o}{X(t)Y(t)Z(t)} \right) e^{\left( \frac{-x^2}{2X(t)^2} - \frac{y^2}{2Y(t)^2} - \frac{z^2}{2Z(t)^2} \right)} \] (5.2)

where \( T_o \) is the isothermal temperature of the plasma. The expression for the position and time dependent velocity \((v)\) of the plasma is given by [94];

\[ v(x, y, z, t) = \frac{x}{X(t)} \left( \frac{dX(t)}{dt} \right) i + \frac{x}{Y(t)} \left( \frac{dY(t)}{dt} \right) j + \frac{x}{Z(t)} \left( \frac{dZ(t)}{dt} \right) k \] (5.3)

where \( dX/dt, dY/dt, \) and \( dZ/dt \) refer to the expansion velocities of the plasma edges \( X, Y, \) and \( Z \) respectively. The equation of gas dynamics governing the expansion of the plasma is the equation of continuity expressed as [94];

\[ -\frac{\partial}{\partial t} \int_v \rho dV = \int_S \rho (\vec{\hat{v}} \cdot \hat{N}) d\hat{A} - \frac{\partial}{\partial t} \frac{mn_o t}{\tau} \] (5.4)

where there is an injection of particles into the plasma, and \( V \) denotes the volume, \( S \) is the surface enclosing that volume, and \( \hat{N} \) is the unit normal vector. The density \( \rho \) of the fluid and the mass \( m \) of the atomic species. This equation simple states the conservation of mass for each atomic species. The last term shows the injection of atomic species into the plasma.

The equation of the conservation of linear momentum or the equation of motion can be expressed as [94];
\[
\int \left[ \rho \frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \frac{\partial \rho}{\partial t} + \rho \vec{v} \cdot \nabla \vec{v} + \vec{v} \cdot \nabla P + \rho \vec{v} (\nabla \cdot \vec{v}) + \nabla P \right] dV = 0 \quad (5.5)
\]

If the relations for the velocity, density, and pressure are substituted into the equation of continuity and the equation of motion, the final solution is [94];

\[
X(t) \left( \frac{1}{t} \frac{dX(t)}{dt} + \frac{d^2X(t)}{dt^2} \right) = Y(t) \left( \frac{1}{t} \frac{dY(t)}{dt} + \frac{d^2Y(t)}{dt^2} \right) = Z(t) \left( \frac{1}{t} \frac{dZ(t)}{dt} + \frac{d^2Z(t)}{dt^2} \right) = \frac{k_B T_0}{M}
\]

where \( T_0 \) is the initial plasma temperature, \( M \) is the atomic mass of the plume species, and \( k_B \) is the Boltsmann constant. This equation determines the initial expansion of the three orthogonal plasma edges, see Figure 5.2. The initial dimensions of the plasma in the transverse direction are determined by the irradiated area of the laser spot size and are on the order of millimeters, whereas in the perpendicular direction the dimension is on the order of microns. Since the velocities are controlled by the pressure gradients, the

**Figure 5.2.** Schematic diagram of the (a) laser spot size at the target surface and (b) the plasma volume with the orthogonal edges \((X_o, Y_o, Z_o)\) indicated.
expansion is anisotropic in the direction perpendicular to the target.

The second phase of the process begins after the termination of the laser pulse \((t > \tau)\), no particles are evaporated or injected into the plasma, also adiabatic expansion of the plasma occurs. The temperature of the plasma can be related to the dimensions of the plasma by the adiabatic thermodynamic equation given by [94]:

\[
T[X(t)Y(t)Z(t)]^{\gamma-1} = \text{const}
\]  

(5.7)

where \(\gamma\) is the ratio of the specific heat capacities at constant pressure and volume where;

\[
\gamma = \frac{C_p}{C_v}
\]  

(5.8)

The thermal energy is rapidly converted into kinetic energy with the plasma attaining extremely high expansion velocities. Since there is no injection of particles into the plasma in this regime, the density and pressure gradients can be expressed in a form similar to equations (5.1) and (5.2) by neglecting the term \((t/\tau)\). The plasma density can be then expressed as [94];

\[
n(x,y,z,t) = \left[ \frac{n_o}{X(t)Y(t)Z(t)} \right] e^{-\left(\frac{x^2}{2X(t)^2} + \frac{y^2}{2Y(t)^2} + \frac{z^2}{2Z(t)^2}\right)}
\]  

(5.9)

and the pressure as [94];

\[
P(x,y,z,t) = \left( \frac{n_o T_o}{X(t)Y(t)Z(t)} \right) e^{-\left(\frac{x^2}{2X(t)^2} + \frac{y^2}{2Y(t)^2} + \frac{z^2}{2Z(t)^2}\right)}
\]  

(5.10)

for \(t > \tau\). The velocity expression remains similar to equation (5.3) as in the isothermal regime. The adiabatic equation of state is given as [94];

\[
\frac{1}{P} \left[ \frac{\partial P}{\partial t} + \vec{v} \cdot \nabla P \right] - \frac{\gamma}{n} \left[ \frac{\partial n}{\partial t} + \vec{v} \cdot \nabla n \right] = 0
\]  

(5.11)

And the equation of temperature is given by [94];
The assumption is that there are no spatial variations in the plasma temperature, \( \nabla T = 0 \). The equations for the velocity, density, and pressure are substituted into the differential equations, Equations (5.4), (5.5), (5.11), and (5.12). The solution which controls the expansion of the plasma in this regime is given by following set of similarity equations [94];

\[
X(t) \left( \frac{d^2 X}{dt^2} \right) = Y(t) \left( \frac{d^2 Y}{dt^2} \right) = Z(t) \left( \frac{d^2 Z}{dt^2} \right) = \frac{6k_B T_o}{M} \left( \frac{X_o Y_o Z_o}{X(t) Y(t) Z(t)} \right)^{(\gamma - 1)}
\]

These equations facilitate the three-dimensional expansion profile of the laser ablated plume. \( X_o, Y_o, \) and \( Z_o \) are the three initial orthogonal plasma edges (Figure 5.2) after the termination of the laser pulse \( (t = \tau) \sim 30 \) ns FWHM at 1 J/cm\(^2\) with the center of the laser-irradiated spot at spatial coordinates \( (0, 0, 0) \) at time \( t \). The initial perpendicular dimensions \( (x) \) are less than 10 - 100 \( \mu \)m. The expansion velocity and initial acceleration are determined by the dimensions of the plasma. The \( x \)-coordinate is directed perpendicular to the target surface. \( X(t), Y(t), Z(t) \) refer to the spatial coordinates of the expanding plasma in the three orthogonal directions. \( T_o \) is the isothermal temperature of the plasma, \( k_B \) is the Boltzmann constant, \( M \) denotes the atomic mass of the plasma species, and \( \gamma \) is the ratio of the specific heat capacity at constant pressure and volume.

This theoretical model for pulsed laser evaporation was applied to experimental conditions by simultaneously solving the similarity Equations (5.6) and (5.7) in a Maple© 9.50 program to compute the plume density profile as a function of time which is TOF of the evaporated material. The program, Plasma Model.mw, is given in Appendix H. For single laser ablation, which this model was originally designed for,
there is an isothermal regime, which lasts for the duration of the laser pulse (20 – 60 ns), followed by the adiabatic regime. However, modeling the dual-laser ablated plume is complicated by the arrival of the CO₂ laser pulse [68]. There are two distinct stages to the initial isothermal expansion in the dual-laser case. The first stage, during the excimer laser pulse, is modeled similarly to the single laser expansion with a higher temperature corresponding to increased absorption of CO₂ laser energy. After the conclusion of the excimer laser pulse, the continuing absorption of the CO₂ laser by the plasma for approximately 264 ns, due to the longer laser pulse width, without including additional incorporation of material from the target into the plume.

5.2. Application of the Theoretical Model

The previously described model was used to fit the theoretical time and position dependent density relation to the experimental temporal time-of-flight (TOF) profiles obtained during in-situ optical diagnostics which were presented in Chapter 4. The analysis was conducted on data for dual-laser ablation with the combined laser fluences of 1 J/cm² UV and 2 J/cm² IR. The UV irradiation component of the dual-laser ablation, low fluence excimer-only laser fluence of 1 J/cm² was analyzed to determine the enhancement provided by the addition of the CO₂ laser energy. The high fluence excimer-only laser ablation (3 J/cm²) was also calculated and compared due to its laser-target interaction similarity to that of the dual-laser effect.

The input parameters used in the simulation were the; laser spot size, atomic mass of the plasma species, delay time, time-gate, distance from the target surface, plasma velocity components, specific heat ratio (gamma), plasma thickness, and plasma
temperature. The area irradiated by the incident laser pulse into the target surface kept consistent and was measured to be 3 mm high × 2 mm wide, and since the orthogonal edges of the plasma volume are determined from the center of the laser spot then Y = 1.5 mm and Z = 1.0 mm. The atomic masses of the elements of the Ba₈Ga₁₆Ge₃₀ compound are Ba₈ = 137.33, Ga₁₆ = 69.72, Ge₃₀ = 72.59, with a total atomic mass equal to 279.64, so the average of the total atomic mass was used (\( M = 93.21 \)) for the plasma species. The laser pulse duration was used as the delay time. The time-gate was the same as the experimental time-gate condition utilized during in-situ OES. The distance from the target surface was the same on-axis position of the OES optical fiber used during data collection, 0 – 6 mm. The perpendicular plasma velocity (\( v_z \)) was determined for the TOF values; however the were determined by successive iterations of the model to fit the data. The remaining simulation parameters; gamma, plasma thickness, and plasma temperature, were also determined by iterations of the computational model. For those parameters which were not determined by direct experimental measurements, were varied based on practical values reported for PLD and trends similar to physical expectations. These values were in the range of 0.1 – 2.0 cm/\( \mu \)s for transverse velocities \( v_y \) and \( v_z \), 1.1 – 1.67 for gamma, plasma thickness of 10 – 100 \( \mu \)m, and plasma temperatures of 2000 – 40000 K [84]. The transverse velocities are on the low end of the range for single-laser ablation due to the highly-forward directed nature, and on the high end for dual-laser ablation due to the much broader expansion profiles observed during in-situ optical diagnostics, Chapter 4. Gamma is high for low energy, low emission PLD and decreases for higher energy conditions. Low plasma thickness and temperature occur with low energy PLE, and is counter for high energy PLE.
The model calculated the number density of a species passing a certain point in space over a set time interval. This includes the emitting and non-emitting atoms or ions of the species. Thus, the model predicts the total amount of material passing that point. This is ideal for fitting film thickness profiles as previously done by Singh et al. and Mukerjee et al. This makes the model a useful tool in predicting thickness profiles and the degree of expansion, however, the calculated number density does not directly correspond to the light emitted by the material at that point for the same time interval. The agreement between the model and the data falls off as the angle from the optic axis and distance from the source increases. The plasma expansion is thought of as a high-pressure gas expanding into the vacuum. The sustained emission from the plume is a result of collision between the constituents of the plume and the lower pressure gradient of the plasma at the outer edges of the plume will result in fewer collisions resulting in lower emission intensities. Due to this effect, the computational results and experimental data were only compared on-axis and close to the target surface (0 – 6 mm) where the emission is still intense and would have less inherent error as compared to longer distances and far off-axis. The results were also computed for multiple points (2, 4, and 6 mm) for each experimental condition to further improve the output.

The corresponding best theoretical fit curves are shown in Figure 5.3 as the solid black lines and overlaid with the experimental results for TOF from Chapter 4. The very high intensity emission of the high fluence single-laser ablation aided in obtaining good agreement between the experimental and computational results (Figure 5.3b). This helped with determining the affect of adjusting parameters in the model which could be applied when analyzing the results of lower emission data, such as for the single-laser 1 J/cm²
Figure 5.3. TOF profiles and theoretical model fit for single-laser ablation (a) 1 J/cm$^2$, (b) 3 J/cm$^2$, and (c) dual-laser 1 J/cm$^2$ UV + 2 J/cm$^2$ IR. The black line is the model fit.
fluence. Adjustment of the parameters to have the peaks of the profiles occur at the proper times determined accurate simulation of the on-axis velocity ($v_x$), and the broadening of the profile was found to be a factor of the initial transverse velocities ($v_y$ and $v_z$). The results for the velocity, plasma thickness, and plasma temperature, are given in Table 5.1. The single-laser high fluence (3 J/cm$^2$) had the greatest plasma thickness which results in the highly forward directed plume, as discussed in the ICCD imaging section. The dual-laser had a thinner plasma thickness, but a much higher plasma temperature, the combination of which resulted in the highly ionized elemental species in the plume and the broader plume expansion. The ionization of the laser-generated plasma is strongly dependent on the surface and plasma temperature.

### Table 5.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$v$ (cm/μs)</th>
<th>$\gamma$</th>
<th>$t$ (μm)</th>
<th>$T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>0.63</td>
<td>1.53</td>
<td>18</td>
<td>7600</td>
</tr>
<tr>
<td>$S_3$</td>
<td>0.90</td>
<td>1.31</td>
<td>49</td>
<td>14700</td>
</tr>
<tr>
<td>$D_L$</td>
<td>1.56</td>
<td>1.17</td>
<td>39</td>
<td>28400</td>
</tr>
</tbody>
</table>

5.3. Summary

Application of the hydrodynamic modeling of the plasma expansion has successful matched the experimentally obtained TOF profiles. This has allowed determination of the laser-generated plasma thickness and temperature. The high initial plasma temperature of the dual-laser technique was obtained while using modest laser energy densities. This comparatively high plasma temperature is the origin of the higher
ionization which was observed during optical diagnostics, and the higher velocity which leads to higher kinetic energy. These effects are conducive for deposition of high-quality thin films.
CHAPTER 6:

CHARACTERIZATION OF THE $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ THIN FILMS

This is a properties characterization report of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ type-I clathrate thin films deposited by pulsed laser-ablation techniques. Electronic devices, coatings, displays, sensors, optical equipment, and numerous other technologies all depend on the deposition high quality thin films. The thin film growth was evaluated by deposition rate and distribution, film structure which included crystallinity, surface morphology, and composition, and the electric transport properties of the films. The electric transport properties included temperature dependent resistivity, and room-temperature Seebeck coefficient, carrier concentration, and mobility. The concept, parameters, and procedure (Appendix I) of the pulsed dual-laser deposition system(s) utilized in the experiments was described in Chapter 1.2 and Chapter 2, with a system diagram shown in Figure 2.1.

6.1. Film Deposition Profile

The dependence of the on-axis film deposition rate, on the laser fluence was investigated. The deposited film thickness was obtained using a surface texture profilometer (Dektak 3030 ST). The step height produced by the removable stainless steel mask is measured by a stylus in contact with, and gently dragging along, the surface of the substrate. For each trial, the target-substrate distance was maintained at 4 cm, and the substrate heater-block was unheated, referred to as room-temperature. The on-axis
The single laser deposition rate increases linearly for fluences from 0.6 to 3 J/cm² at a rate of 0.55 Å/pulse per J/cm² (Figure 6.1). The ablation threshold occurred at fluences lower than 0.6 J/cm² where no detectable deposition occurred. The ablation threshold occurs at the value where the energy density is absorbed into the material but is not sufficient to raise the temperature of the material enough to cause evaporation. Whereas on the other end of the linear increase of the deposition rate (≥ 3 J/cm²), the laser ablation causes the plasma density at the surface of the target to reach a point where higher laser fluences can not penetrate the plasma, thereby shielding the target from further evaporation. At this point the deposition rate saturates. At this high energy region, changes in the plasma may have occurred such as plasma losses and reflectivity of the laser pulse. The on-axis deposition
rate of 0.14 ± 0.03 Å/pulse for preliminary dual-laser ablation conditions (1 J/cm² UV and 2 J/cm² IR) was found to be significantly lower than the excimer-only depositions. The relatively low deposition rate is a result of the combination of low laser fluences, and other factors unique to dual-laser ablation such as the broader expansion profile which was presented in Chapter 4.

Large area films depositions were performed for dual-laser (1 J/cm² UV + 2 J/cm² IR) (DL) and the excimer-only conditions of 1 J/cm² (S₁) and 3 J/cm² (S₃). The xyz axis orientation of the irradiated laser spot on the target surface relative to the resulting film deposition on the substrate is illustrated in the schematic diagram shown in Figure 6.2. The x-axis refers to the central axis of the laser spot, the laser-generated plume of material, and the peak of the film distribution profile. This x-axis is perpendicular to the surface of the target and the substrate (Figure 6.2). The film thickness profiles of these films (Figure 6.3) along the y-axis (vertical) and z-axis (horizontal) of the various laser fluences illustrate the broader deposition profile achieved by the dual-laser configuration. The solid line is the \( \cos^n(\theta) \) fit for the profiles, where \( \theta \) corresponds to the angle between

![Figure 6.2](image-url)

**Figure 6.2.** A schematic diagram illustrating the xyz axis orientation of the irradiated laser spot on the target surface relative to the resulting film deposition on the substrate.
Figure 6.3. Profile film thickness along the (a) z-axis and (b) y-axis for Ba$_8$Ga$_{16}$Ge$_{30}$ deposited on quartz substrates. The target to substrate distance was 4 cm. The solid lines indicate the theoretical fit $\cos^2\theta$. 
the radial vector and the target normal. Depending on the pulse energy density and other parameters, the thickness variation across the films typically show a relationship where \( n = 8-12 \) [94]. The \( \cos^n(\theta) \) fit for the profiles is summarized in Table 6.1. The \( y/z \) ratio for the \( \cos^n(\theta) \) approaches unity for dual-laser indicating a broader and more uniform distribution profile. This ratio progresses to a value of 2 as the single-laser fluence increases, which is indicative a narrower, more forward directed deposition. The lower on-axis deposition rate discussed earlier for the dual-laser deposition is a result of its desirable broader deposition as compared to the single-laser conditions.

**Table 6.1.** The \( n \) factor of the \( \cos^n \theta \) fit for the \( y\)- and \( z\)-axis thickness profiles for single and dual-laser depositions at a target-substrate distance of 4 cm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( n ) factor for ( \cos^n(\Theta) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( z )</td>
</tr>
<tr>
<td>Single 1 J/cm(^2)</td>
<td>9.0</td>
</tr>
<tr>
<td>Single 3 J/cm(^2)</td>
<td>8.5</td>
</tr>
<tr>
<td>Dual-Laser</td>
<td>7.0</td>
</tr>
</tbody>
</table>

6.2. Thin Film Surface Morphology

The surface topography of the excimer laser deposited films was examined by SEM. An example of the distribution of undesired particulates found on the films is shown in the 3000X magnified SEM image (Figure 6.4). The films were deposited at excimer-only laser fluences of 1 and 3 J/cm\(^2\) and dual-laser fluences of 1 J/cm\(^2\) UV + 2J/cm\(^2\) IR. The films deposited by excimer only single-laser ablation have an undesirable range of particulates ranging from sub-micron droplets to macro molten droplets, with
sizes greater than 5 µm, and irregular shards, Figure 6.5a and b, as seen previously [75, 99, 100] and with other TE materials [45]. The macro droplets originate from splashing of the irradiated target molten layer which results in particles which were molten in transit but too massive to vaporize in the laser generated plasma, these features are typical of high fluence ablation of materials composed of metallic elements. A common and simple approach to reduce the quantity of particles is to decrease the laser fluence, so films deposited with a fluence of 1 J/cm² (Figure 6.5a) do not contain macro droplets but the micron to submicron sized particles are still present. However, the film deposited by dual-laser ablation resulted in a significant reduction in particulates (Figure 6.5c).

Figure 6.4. A SEM at 3000 times magnification which shows examples of the various types of particulates found on the thin films.
Figure 6.5. SEM images of thin films deposited by single-laser PLD with fluences of (a) 1 J/cm$^2$ and (b) 3 J/cm$^2$, and dual-laser fluences of (c) 1 J/cm$^2$ UV and 2 J/cm$^2$ IR.
Thin films were deposited at three distinct $p$-$p$ delays of -25 ns, 100 ns, and 175 ns, respectively, to investigate the effect on the morphology of the films. At -25 ns $p$-$p$ delay, a significant portion of the CO$_2$ laser pulse arrives at the target surface before the arrival of the excimer laser pulse (Figure 6.6) resulting in a condition referred to as pre-melt of the laser-target interaction site. Based on the results presented in Chapter 4, 100 ns $p$-$p$ delay was a delay at which expansion of the plasma and plume are increased. When the $p$-$p$ delay is 175 ns, plasma and/or plume pumping occurs. Upon inspection of the deposited films by SEM (Figure 6.7a and 6.7c) the films produced under the conditions with the -25 ns and 175 ns $p$-$p$ delays, respectively, have a large amount of molten droplets, an undesirable quality for the deposition of thin films. However, the 100 ns $p$-$p$ delay film (Figure 6.7b) is smooth with few sub-micron sized particles. The particulates in Figure 6.7a have been ejected from the target surface and only partially melted while

![Figure 6.6. Overlapped oscilloscope traces for the excimer laser pulse (UV) and CO$_2$ laser pulses (IR) for peak-to-peak delays of -25 ns, +100 ns, and +175 ns, relative to the UV pulse at 0 ns.](image-url)
passing through the laser generated plasma. The particulates in Figure 6.7c are characteristic of ejected material that has not reached a temperature to vaporize the material but enough to liquefy the material resulting in molten droplets that splash when deposited on the substrate.

Implementing the dual-laser technique has greatly reduced the quantity of particulates on the film, as can be seen in Figure 6.7b. Dual-laser ablation has eliminated the large macro droplets through laser-target interaction site pre-melt from the long wavelength IR CO2 laser followed by UV laser ablation from pre-smoothed target zone, then submicron sized particles are evaporated in the plasma which has been increased in temperature due to absorption of the remainder of the long CO2 laser pulse.
Figure 6.7. Scanning electron micrographs of films deposited at various dual-laser peak-to-peak delays with 1 J/cm² UV and 2 J/cm² IR laser fluences. The CO₂ laser pulse peak is delayed by (a) -25 ns, (b) 100 ns, and (c) 175 ns, relative to the excimer laser pulse peak. The film deposited at 100 ns delay resulted in reduced particulate generation.
6.3. Thin Film Crystallinity

The crystallinity of the deposited thin-films was examined by x-ray diffraction (XRD). The XRD peak intensity dependence on the substrate temperature was investigated over a range from room temperature to 500 °C as shown in Figure 6.8. The excimer laser fluence was maintained at 1 J/cm². The germanium impurity peak at 27.27° only appears at 500 °C when the film quality appears to be affected by the deposition temperature, and the deposition rate is reduced as the material is re-evaporated from the heated substrate. The XRD intensity of the prominent peak at 31.2° (321) as a function of temperature is shown in Figure 6.9 and a maximum occurs at a substrate temperature of 400 °C, and may be near an optimal deposition temperature for this laser fluence.

![Figure 6.8](image-url)

**Figure 6.8.** The XRD dependence on the substrate temperature. The excimer laser fluence was 1 J/cm².
The XRD peak intensity dependence on the excimer laser fluence was investigated over a range of 1 to 6 J/cm², as shown in Figure 6.10. The substrate temperature was maintained at 400 °C. The germanium impurity peak at 27.27° does not appear in any of the films. The XRD pattern was indexed to a cubic unit cell structure with space group Pm-3m. The diffraction pattern displays peaks which are characteristic of type-I clathrates and are in good agreement those reported for Ba₅Ga₁₆Ge₃₀ [76, 79] and for the target as reported in Chapter 3. For each of the fluences, the peak that occurs at 29.85° (320) is proportionately lower than that of the target. The XRD intensity of the prominent peak at 31.2° (321) as a function of excimer laser fluence is shown in Figure 6.11. The peak intensity increases linearly from 1 to 3 J/cm² and a maximum occurs at a fluence of 4 J/cm².

**Figure 6.9.** XRD intensity of the peak 31.2° (321) as a function of temperature.
Figure 6.10. The XRD patterns dependence on the excimer laser fluence. The substrate temperature was 400 °C.

Figure 6.11. XRD intensity of the peak 31.2° (321) as a function of the excimer laser fluence.
A set of films were deposited by dual-laser ablation with matching thickness of 264 nm for single-laser films, Figure 6.12. It is evident that the low fluence deposited film has a weak XRD peak intensity as compared to the other configurations (29% max.). The XRD peak patterns of the films deposited by the high fluence single-laser and the dual-laser configurations agree with that produced by the Ba₈Ga₁₆Ge₃₀ target [79]. These two films have similar XRD peak heights even though the films grown by the dual-laser deposition technique only required a substrate temperature of 300 °C as compared to 400 °C for the single-laser deposited films. This is achieved by the increased ionization and kinetic energy of the plume material provided by the dual-laser ablation leading to higher mobility of the material arriving at the heated substrate.

Figure 6.12. X-ray diffraction patterns for single-laser 1 J/cm² UV (S₁₁) and 3 J/cm² UV (S₁₃), and dual-laser (D₁₁₂) 1J/cm² UV + 2 J/cm² IR. The film thickness was 267 ± 30 nm. The type-I clathrate XRD peaks are identified to a cubic unit cell structure with space group Pm-3n.
6.4. Thin Film Composition

The composition of the deposited thin-films was analyzed by energy dispersive X-ray spectroscopy (EDS), a standard procedure for identifying and quantifying the elemental composition of sample volumes as small as a few cubic micrometers (Appendix J). The dependence of the film stoichiometry on the excimer laser fluence was examined. The quartz substrate temperature was maintained at 400 °C. The laser fluence was varied from 1 to 6 J/cm². The average film thickness was 5780 ± 780 Å. The atomic percentage ratios normalized to Ba₈ are shown in Figure 6.13. The deposition over the fluence range of 1 to 6 J/cm² produced the desired stoichiometry of Ba₈Ga₁₆Ge₃₀.

![Figure 6.13](image_url)

**Figure 6.13.** EDS quantification of the films deposited as a function of the excimer laser fluence.
Films were deposited by the dual-laser ablation technique along with comparative single-laser deposited films. The films presented had an average thickness of 267 ± 30 nm. The film deposited by the single-laser 1 J/cm² fluence has slight Ba enrichment as compared to the Ga and Ge content. This is a result of the preferential evaporation of the more volatile Ba from the target, Table 6.2, leading to a greater percentage of Ba arriving at the substrate. It is noted that the deviation in the low fluence deposited film was much greater than the other two configurations. The on-axis stoichiometry of films deposited by the single-laser 3 J/cm² fluence and dual-laser are with the proper range as the outcome of phase segregation during ablation from the target. The Ga/Ge ratio of these two depositions resulted in an n-type composition ratios (Ga/Ge < 0.533) with the high fluence single-laser closer to intrinsic [6].

Table 6.2. Stoichiometry of thin films deposited by single-laser 1 J/cm² (S₁) and 3 J/cm² (S₃), and dual-laser (Dual) ablation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic %</th>
<th>Ga/Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba</td>
<td>Ga</td>
</tr>
<tr>
<td>Balanced</td>
<td>8.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Dual</td>
<td>8.1±0.4</td>
<td>15.3±0.2</td>
</tr>
<tr>
<td>S₃</td>
<td>8.1±0.4</td>
<td>15.7±0.6</td>
</tr>
<tr>
<td>S₁</td>
<td>8.5±0.6</td>
<td>16.3±1.2</td>
</tr>
</tbody>
</table>

The composition of the dual-laser deposited films with various p-p delays was investigated and the elemental composition summary of these deposited films (Table 6.3) reveals that the -25 ns and 175 ns films are far off the Ba:Ga:Ge 8:16:30 intrinsic ratio. These films are rich in barium and gallium, the elements with the lowest boiling points of the three. The film thicknesses are also increased as a result of increased material being
ejected from the target surface, in vapor and liquefied form. The slightly more forward directed plume propagation, as indicated by the narrower and more intense plasma expansion will also contribute to higher on-axis material deposition. Although this experiment exaggerated non-optimum laser pulse synchronization by 75 ns and greater, it demonstrates the need proper synchronization the dual-laser pulses for optimum energy coupling of the CO$_2$ laser pulse into the excimer laser generated plume. It also leads to possibility of tailoring the elemental ratios through proper management laser energies and the $p$-$p$ delay. This could be a future investigation of this complex material for control of the Ga:Ge ratio for $p$-type and $n$-type film growths.

### Table 6.3. Barium, gallium, and germanium composition of thin-films deposited a various dual-laser peak-to-peak delays of 175 ns, 100 ns and -25 ns. The substrate temperature during deposition was room temperature. The thickness of the resultant films is given.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic %</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba</td>
<td>Ga</td>
</tr>
<tr>
<td>175 ns</td>
<td>17.5±1.4</td>
<td>22.2±4.7</td>
</tr>
<tr>
<td>100 ns</td>
<td>8.7±0.1</td>
<td>16.0±0.1</td>
</tr>
<tr>
<td>-25 ns</td>
<td>47.5±4.5</td>
<td>26.7±16.8</td>
</tr>
</tbody>
</table>

6.5. Electric Transport Properties

The thin films were further characterized by their electric transport properties. Samples deposited by single and dual-laser to various thicknesses of 200 to 650 nm were evaluated. The electric transport properties of the films included temperature dependent resistivity ($\rho$), carrier concentration ($n$), thermopower or Seebeck coefficient ($S$), and thermoelectric power factor ($S^2/\rho$).
6.5.1. Temperature Dependant Resistivity

The temperature dependent resistivity of the films was measured using standard a four-point probe technique. The film was mounted in a closed cycle refrigeration system that controlled the temperature in the range starting at 320 K and was decreased to 20 K. The resistance was typically measured across a 0.20 cm × 0.31 cm bridge that was scribed on the film. Voltage measurements were taken for injected currents of 5 to 1000 μA, determined upon the response of the particular thin film sample. A sample

![Graph showing temperature dependent resistivity](image)

**Figure 6.14.** The temperature dependent resistivity of a Ba₈Ga₁₆Ge₃₀ thin film sample at various applied injection currents, demonstrating the semiconducting behavior.

temperature dependent resistivity result for a random Ba₈Ga₁₆Ge₃₀ thin film is shown in Figure 6.14. The resistivity increases exponentially with decreasing temperature to demonstrating the semiconducting characteristic of the deposited material. The resistivity of this particular sample diverges as the temperature is decreased due to ohmic heating as
a result of the high resistivity and applied current. This effect is avoided during final sample measurements. During this investigation it was found that films deposited by the excimer-only single-laser ablation fluence of 1 J/cm$^2$ had excessively high resistivity, beyond the limits of the available instrumentation, so this configuration was eliminated from further electric transport characterization. Thin films deposited by high fluence single-laser ablation (3 J/cm$^2$) were also found to have high but measureable resistivity, and were included in the following investigations as a comparison to the results of the higher quality dual-laser deposited thin films. Although the high fluence single-laser deposited films had high particulate concentrations as compared to the dual-laser deposited films, the crystallinity results were comparable and of interest, as discussed in Sections 6.3 and 6.4 of this chapter.

The temperature dependent resistivity was investigated for films of various thicknesses to gain insight into the quality of the films. Films deposited to a thickness range 200 to 650 nm are presented and the results are shown in Figure 6.15. As the thickness of the film increased the resistivity decreased for the dual-laser deposited samples. However the high fluence single-laser film at 300 nm thick show the highest resistivity and thicker films resulted in increased resistivity counter-intuitive to typical findings. These thicker single-laser deposited films were imaged by SEM and were found to contain micro-cracks (Figure 6.16) causing discontinuity and increased resistance. These micro-cracks are the result of stress in the film; however the film did not peel from the substrate indicating adequate adhesion. These micro-cracks did not occur with the dual-laser deposited thin-films, again demonstrating the benefit of the technique by reducing the stress in the film through the highly energetic and ionized plume of material.
created during ablation, as discussed in Chapters 4 and 5. In general, films are in a state of stress, compressive or tensile stress. Compressively stressed films will expand parallel to the substrate, while tensile stressed films will contract. This stress can lead to the formation of micro-cracks, as seen in Figure 6.16.

**Figure 6.15.** Temperature dependent resistivity of the Ba$_8$Ga$_{16}$Ge$_{30}$ thin films deposited by single and dual-laser ablation for various thicknesses.

**Figure 6.16.** A scanning electron micrograph image of a film deposited by single-laser PLD with a fluence of 3 J/cm$^2$. The average film thickness is 623 nm. The micro-cracks are visible on the film.
to the substrate surface leading to peeling. Tensile stressed films want to contract and will crack if the elastic limit of the material is surpassed. High stress in films is undesirable for device applications because they (a) tend to have poor adhesion, (b) are susceptible to corrosion, (c) tend to crack, and (d) have resistivity higher than ‘relaxed’ annealed films [134].

During the SEM investigation of these films it was found that the highly resistive films grown by single-laser deposition display the occurrence of ‘crystallites’ within the films, as seen in Figure 6.17a (d). These ‘crystallites’ are 50 to 150 nm in diameter and appear to not be in contact with one another. The films deposited by dual-laser ablation do not show this effect, as see in the SEM image of Figure 6.17b (d). Thin films formed by physical vapor deposition methods such as PLD grow by condensation of atoms or molecules from the vapor phase. This condensation begins with the formation of small clusters or nuclei through random agglomeration, as depicted in Figure 6.17a (a) and Figure 6.17b (a). Atoms may continue to move along the surface into other positions as a result of the kinetic energy associated with the material’s arrival velocity or by thermal activation from the heated substrate. The dual-laser deposited material has a higher velocity as discussed in Chapter 4, 0.90 and 1.56 cm/µs for high fluence single-laser and dual-laser ablation, respectively. The dual-laser ablation results in higher surface mobility possibly allowing increased migration, leading to smaller and more numerous initial nucleation sites, resulting in a more uniform film growth as opposed to that of the single-laser ablation results. As depicted in the progression of nucleation and growth, as shown in Figures 6.17a (a-c) and 6.17b (a-c).
Figure 6.17a. Schematic diagram of progressive film nucleation for single-laser deposition, (a) sparse nucleation, (b) increased coalescence growth, (c) final, discontinuous crystal growth within an amorphous fill and or channels and holes, and (d) an SEM image of a Ba$_8$Ga$_{16}$Ge$_{30}$ film grown with 3 J/cm$^2$ single-laser ablation. Note the 50-150 nm ‘crystallites’ encased within the film growth.

Figure 6.17b. Schematic diagram of progressive film nucleation for dual-laser deposition, (a) high energy, ion bombardment promoting increased nucleation, (b) increased, dense crystal growth, (c) final, uniform continuous growth, and (d) an SEM image of a Ba$_8$Ga$_{16}$Ge$_{30}$ film grown from 1 J/cm$^2$ UV and 2 J/cm$^2$ IR dual-laser ablation. Note the smooth film growth as compared to the image in Figure 6.20a.
The electrical conductivity of a material is due to the motion of charge carriers through the lattice [135]. These carriers are affected by non-periodicity in the lattice, resulting lattice vibrations, lattice defects, impurities, vacancies, interstitials, dislocations, grain boundaries, and alloying. The resistivity of thin films is generally higher than that of the same bulk material, resulting from the fact that films generally contain more defects, dislocations, and grain boundaries [134]. The addition of even small amounts of an impurity, such as oxygen, can cause very large changes in resistivity, on the order of several orders of magnitude. Vacancies, interstitials, and dislocations are considered to have a smaller effect on the resistivity of a material [136]. These issues may be factors in the resistivity values obtained for high fluence single-laser deposited films as compared to the dual-laser results. They may also become an increasing contribution to the dual-laser deposited films as the films were made thinner. The room-temperature results obtained by the temperature dependent resistivity investigation are summarized in Table 6.4

<table>
<thead>
<tr>
<th>Sample</th>
<th>PLD</th>
<th>Fluence $d$</th>
<th>$d$ (nm)</th>
<th>$\rho$ (m$\Omega$·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single 3 UV</td>
<td>300</td>
<td>$6.54 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Dual 1 UV + 2 IR</td>
<td>202</td>
<td>$3.48 \times 10^3$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Dual 1 UV + 2 IR</td>
<td>269</td>
<td>$1.61 \times 10^3$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Dual 1 UV + 2 IR</td>
<td>435</td>
<td>$4.55 \times 10^2$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Dual 1 UV + 2 IR</td>
<td>632</td>
<td>$2.30 \times 10^1$</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4. Temperature dependent resistivity results of the Ba$_8$Ga$_{16}$Ge$_{30}$ thin films deposited by single and dual-laser ablation for various thicknesses.
6.5.2. Van der Pauw - Hall Measurement

Electrical properties of the thin films were measured using the Van der Pauw technique. Since the thickness of the films was much smaller than the length and width of the sample and grown on symmetrical (½ × ½ inch) quartz substrates, the Van der Pauw method could be successfully applied. The electrical contacts were made using silver epoxy and thin, epoxy coated, copper wire. They were placed on the corners of the film as shown in the schematic diagram (Figure 6.18). During the Hall measurements, the magnetic field \( B \) was applied perpendicular to the film plane as shown in the schematic diagram (Figure 6.18). The electromagnet utilized for the measurements provided a maximum field of 0.5 Telsa.

The results were tabulated such that the sheet resistance \( R_s \) was determined by:

\[
e^{(-\sigma d / R_s)} + e^{(-\sigma d / R_s)} = 1
\]  
[6.1]

The resistivity \( \rho \) could then be calculated using the film thickness \( d \):

\[
\rho = R_s d
\]  
[6.2]

The carrier concentration \( n \) could then be determined using:
\[ n_S = \frac{8 \times 10^{-8} |I_B|}{q \sum V_i} \]  

[6.3]

\[ n = \frac{n_S}{d} \]  

[6.4]

The mobility \((\mu_H)\) was then calculated using the following:

\[ \mu_H = \frac{1}{q n_S R_S} \]  

[6.5]

<table>
<thead>
<tr>
<th>Sample</th>
<th>PLD</th>
<th>Fluence (J/cm²)</th>
<th>(d) (nm)</th>
<th>(\rho) (mΩ·cm)</th>
<th>(n) (cm⁻³)</th>
<th>(\mu_H) (cm²/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single</td>
<td>3 UV</td>
<td>300</td>
<td>6.7×10⁴</td>
<td>3.4×10¹⁶</td>
<td>10.2</td>
</tr>
<tr>
<td>2</td>
<td>Dual</td>
<td>1 UV + 2 IR</td>
<td>202</td>
<td>3.58×10³</td>
<td>9.9×10¹⁶</td>
<td>17.7</td>
</tr>
<tr>
<td>3</td>
<td>Dual</td>
<td>1 UV + 2 IR</td>
<td>269</td>
<td>1.60×10³</td>
<td>5.6×10¹⁶</td>
<td>17.1</td>
</tr>
<tr>
<td>4</td>
<td>Dual</td>
<td>1 UV + 2 IR</td>
<td>435</td>
<td>4.31×10²</td>
<td>1.4×10¹⁸</td>
<td>5.5</td>
</tr>
<tr>
<td>5</td>
<td>Dual</td>
<td>1 UV + 2 IR</td>
<td>632</td>
<td>2.10×10¹</td>
<td>1.1×10¹⁹</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Table 6.5. Results of the Van der Pauw measurements for room temperature resistivity \((\rho)\), carrier concentration \((n)\), and mobility \((\mu_H)\).

Results of investigating films of various thickness using the Van der Pauw method for room temperature resistivity \((\rho)\), carrier concentration \((n)\), and mobility \((\mu_H)\) are summarized in Table 6.5. Values of 1 to 52 mΩ·cm for bulk polycrystalline \(\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}\) at room-temperature have been reported [101, 33]. The carrier concentrations \((n)\) are lower than that reported for the bulk \(\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}\) material, typical for thin films. However, the thinner films resulted in excessively low calculation of carrier concentration due to unaccounted thickness variations. Average film thickness does not accurately correspond to calculations and further investigation is required.
6.5.3. Seebeck Coefficient

Thermoelectric energy conversion can be discussed with reference to the schematic of a thermocouple configuration shown in Figure 6.19. It can be considered as a circuit formed from two dissimilar conductors \( a \) and \( b \) which are connected electrically in series but thermally in parallel. If junctions at 1 and 2 are maintained at different temperatures \( T_H \) and \( T_L \) where \( T_H > T_L \), an open circuit electromotive force (emf), \( V \) is developed between 3 and 4 and given by \( V = \alpha(T_H - T_L) \) or \( \alpha = V/\Delta T \), which defines the differential Seebeck coefficient \( \alpha_{ab} \) between elements \( a \) and \( b \). For small temperature differences the relationship is linear. The sign of \( \alpha \) is positive if the emf causes a current to flow in a clockwise direction around the circuit and is measured in units of V/K, or more often in µV/K [110]. The Seebeck coefficient or thermopower, \( \alpha \), is an intrinsic and bulk property of a material related to the material’s electronic structure and is not geometry specific [106, 107]. The thermopower yields information about the sign (+/-) of the charge carrier and is essentially the entropy per carrier divided by the charge of the carrier [106]. When a thermoelectric material is subjected to a small and constant temperature difference, a thermoelectric potential difference is produced. The thermopower of the material is defined as \( \alpha = \Delta V/\Delta T \) as \( \Delta T \rightarrow 0 \) [108] given by a measurement of the ratio of the sample voltage (electric field) to the temperature difference (temperature gradient) along the sample;
where \( \alpha_{ab} = \alpha_b - \alpha_a \) is the measured value of the thermopower which includes both the sample contribution, \( \alpha_a \), as well as the measurement lead contribution, \( \alpha_b \). The lead contribution, typically Au, Cu, or Chromel, must be known and subtracted from each data point at each temperature [106] such that the thermopower of the sample \( \alpha_a = \alpha_b - \alpha_{ab} \) and equation 6.1 may be rewritten as;

\[
\alpha_a = \frac{\Delta V}{\Delta T} = \frac{(V_H - V_L)/(T_H - T_L)}
\]

An essential requirement for accurate thermopower measurement but also a source of error is the determination of the temperatures \( (T_H \text{ and } T_L) \) and voltages \( (V_H \text{ and } V_L) \) at the same positions, respectively. This requires the contact junction of the temperature probe to be located as close as possible to the voltage probe junction. A way to minimize this error is to use one leg of each thermocouple as the sample voltage lead itself, thus the thermocouples act both as voltage potential leads and for measuring the thermo-voltage [106]. Another requirement is zero heat flow along the measuring leads where the leads act as heat sinks [108]. This can be minimized by utilizing leads with as small a diameter as practical.

Figure 6.19. A schematic diagram of a basic thermocouple arrangement (a-b) between hot \( (T_H) \) and cold \( (T_L) \) sources.
The simplest technique of measuring the thermopower is the small $\Delta T$ method [106]. Typically, the temperature difference should be as small as possible by definition ($\alpha = \Delta V/\Delta T$ as $\Delta T \to 0$), but in practice a compromise has to be met in achieving sufficient measurement accuracy, thus $\Delta T$ is usually of the order of 1 to 5 K [108]. This method involves sweeping the $\Delta T$ around a set temperature and measuring the resulting voltage of the sample. The slope of $\Delta V$ as a function of $\Delta T$ is the measured thermopower $\alpha_{ab}$. It is required that $\Delta V$ is linear in $\Delta T$ and goes through $\Delta V = 0$ at $\Delta T = 0$ [106].

For accurate and reproducible determination of the thermopower, the temperature difference should be relatively small, the specimen homogeneous, and spurious voltages of thermal origin should be eliminated. When measuring at temperatures far from ambient, spurious thermally induced voltages will become more significant in the measuring circuit. It maybe also necessary to take into account the absolute thermopower of the contact material used to thermally anchor the leads to the sample, especially if this is comparable to that of the material being measured. To minimize such effects it is recommended to measure the thermoelectric potential difference as a function of temperature difference, the slope of the curve (d$\Delta V$/d$\Delta T$) thus giving the overall thermopower [108].

Measurement of the thermopower of thin-film samples on substrates requires special consideration. The thermal conductivity of the substrate is typically quite high and can be a source of unwanted temperature gradients. Thermally anchoring the thermocouple bead to the film surface presents sources of error since only a small fraction of the bead surface can actually be placed in contact with the film surface. In order to assure that the remainder of the bead is at the same temperature, solder or a
thermally conducting epoxy can be used to thermally anchor the entire bead to the film [107].

It has been shown that there are a number of sources for error. It is quite easy to get an erroneous sign (+/-) of the thermopower, it is essential to use consistency in defining the direction of the temperature gradient with respect to the voltage measurement, the sample will typically be opposite in sign from the measured thermopower. This is due to the fact that one has to subtract out the lead contributions ($\alpha_a = \alpha_b - \alpha_{ab}$) which is usually small compared to the sample thermopower [107]. The voltage leads must be in excellent thermal contact to the point at which the temperature is measured [107]. High resistance contacts can exhibit ac pickup resulting in a rectified dc offset voltage which can also lead to errors [106]. The temperature dependence of the thermopower can be quite difficult to interpret, many contributions, such as phonon drag can be involved in combination with simple diffusion thermopower (linear in $T$) which is typical of metals [106].

To check the accuracy of a Seebeck measurement both a constant offset and errors proportional to the Seebeck coefficient of the sample have to be excluded. Thus, Seebeck calibration with reference materials should include a pure metal with low Seebeck coefficient (few $\mu$V/K like Pt, Pd, Cu or others) as well as a reference material with higher Seebeck coefficient (preferentially several 10 to 100 $\mu$V/K) this could be CuNi (constantan) or NiCr (chromel) based on standardized thermocouples’ calibration values [108].

A popular method to measure thermopower is the differential method, shown schematically in Figure 6.16. In this method, the temperature difference $\Delta T$ between two
points of the sample and the potential difference $\Delta V$ between the same two points is measured when the net current in the sample is zero, $I = 0$. Therefore, the electrical field in the sample is due to the thermopower only, $E = \alpha \Delta T$ [109].

Figure 6.20 shows two thermocouples in contact with the surface of the solid whose Seebeck coefficient is to be measured. The temperature of junction X is raised above ambient temperature and is assumed that the sample immediately below the junction is at the same temperature, namely $T_H$. Likewise it is assumed that $T_L$ is the temperature both of the junction Y and the solid immediately beneath it. The thermoelectric potential measured between wires 1 and 3 or 2 and 4 will depend only upon the nature of the wires (C or A), the nature of the sample, and the temperature difference $T_H - T_L$: the potential is independent of the shape of the isotherms between X and Y. If the potential difference is measured using the wire C (1 and 3), then the mean Seebeck coefficient $S_{SC}$ of the sample over the small temperature interval $T_H$ to $T_L$, is given by where $S_C$ is the absolute mean Seebeck coefficient of material C between $T_H$ and $T_L$. The sign of $V$ is given by the sign of the potential of the cold electrode, and the
appropriate sign of the material C must be used for $S_C$. For p-type material the Seebeck coefficient is positive (+), and so $V$ will be positive, even for very low values of $S_S C$, provided $S_C$ is chosen as positive [111].

In many applications an automatic ice bath with built-in reference thermocouples (T/C’s) may not be practical. Automatic ice baths are expensive and do not operate reliably in ambient temperatures below 0.0 °C or above 40.0 °C. Instruments available today for T/C measurement provide and electronic circuit for determining the temperature of the terminals to which the T/C’s are attached. An appropriate reference voltage is added by the system to that produced by the external T/C. Such circuits are referred to as compensators, because they compensated for the fact that the terminals to which the T/C’s were connected were not at the ice-point temperature. The compensator produces a voltage that is a function of the terminal temperature [112].

One of the main challenges is the measurement of true temperature gradient across the sample. A true temperature gradient is measured only when good thermal contact is made between the sample and the sensors. In case of poor thermal contact, the temperature drop at the interface will underestimate $\alpha$, due to overestimation of $\Delta T$. The only way to reduce this error is to reduce the heat flow that is necessary to develop the required temperature gradient $\Delta T$. In other words, one needs to use a long thin sample. Alternatively, one can attach thin thermocouples directly on the sample. In this case, finite area contact introduces error to that extent. In addition, samples that exhibit low thermal conductivity tend to give more accurate values. However, it is not always possible to obtain a sample of desired dimensions or thermal conductivity [113]. It has
been reported, that it is necessary to select the metal electrode fitted to the thermoelectric material to make the thermoelectric conversion efficiency as high as possible [114].

It has been reported of the existence of a universal optimal reduced Fermi potential ($\eta_{\text{opt}}$) and the corresponding optimal Seebeck coefficient, in the range of 103-187 $\mu$V/K, where the power factor is maximized at any given temperature. These findings help to dispel the notion that good thermoelectrics should have very large $|S|$. Instead, it would help to refocus efforts on increasing the power factor ($S^2\sigma$) through an increase in the conductivity while maintaining $|S|$ ~ $S_{\text{opt}}$. Additionally, the identification of $\eta_{\text{opt}}$ will enable easy determination of the optimal carrier concentration [115].

Simple, rapid, versatile, accurate techniques for determining the Seebeck coefficient of thermoelectric materials along with experimental difficulties have been described in publications [111, 116-118]. The Seebeck coefficient data for materials, especially semiconductors, are prone to variation because of their sensitivity to the exact material composition. Also, the temperature dependency can be significant, for example a 5-10% increase for metals over a temperature rise of 30 °C [118]. A main problem in surface temperature measurement is getting the thermocouple in good thermal contact at the chosen location. Always use the smallest diameter thermocouple wire that can be handled without too much breakage [120].

6.5.3.1. Seebeck Apparatus

A differential method was chosen for the determination of the Seebeck coefficient. This method depends on the temperature difference, $\Delta T$, and potential difference, $\Delta V$, measured between the same two points of the sample when the net
current in the sample is zero, \( I = 0 \). When the net current is zero, the electric field in the sample is only due to the thermopower, \( E = \alpha \Delta T \) [122]. In the apparatus shown in Figure 6.21, the heater blocks are 3.82 cm long \( \times \) 8.82 cm wide \( \times \) 1.33 cm high stainless steel with a 6.14 mm diameter \( \times \) 5.12 cm long, 250 watt stainless steel sheath cartridge heater inserted into the block. The heating elements are secured into the blocks with silver ink to improve thermal contact. The power to each heater block was adjusted by 0 - 120 V AC Variac power supplies and the temperature is measured and monitored with thermocouples. The sample is clamped between two stainless steel blocks with the block-sample contact areas coated with silver ink to improve thermal contact. The temperature probes are bare T-type, copper-constantan, 0.005 inch diameter, 12 inch long thermocouples. The junctions of the thermocouples are adjusted as to maintain their position under slight compression and then a small amount of silver ink, less than 1 mm in diameter, is applied to ensure thermal contact while securing the position. A thermocouple is affixed to each heater block and two on the sample. To minimize temperature fluctuations the apparatus is screened from drafts by an enclosure. The voltage difference is measured between the copper legs of the thermocouples and read by a Keithley 182 Sensitive Digital Voltmeter and displayed on a National Instruments LabVIEW 6.1 program which averages and displays the voltage. A simplified diagram of the Seebeck Coefficient measurement apparatus is shown in Figure 6.22 and a photograph of the apparatus is shown in Figure 6.23 with detail of the thermal couple positioning.

The possible sources of error are compensation error, linearization error, measurement error, thermocouple wire error, and noise error. To minimize errors, the
SCB-68 shielded desktop connector block has a temperature sensor for cold-junction compensation (CJC). The temperature sensor is powered with switches S1, S2, and S3 set for single-ended or differential mode. This configuration also powers the signal conditioning area and circuitry. CJC is accurate only if the temperature sensor reading is close to the actual temperature of the screw terminals. Therefore, when reading the thermocouples, the SCB-68 is kept away from drafts or other temperature gradients, such as those caused by heaters, radiators, fans, and warm equipment [123].
Figure 6.21. A schematic wiring diagram of the apparatus used to measure the temperature gradient and Seebeck voltage, used to determine the Seebeck coefficient.
6.5.3.2. Seebeck Apparatus Characterization

The T-type thermocouples utilized in the Seebeck apparatus were characterized to determine the relative precision of the chosen sensors. A bead of silver ink was placed on heater block 1 and the tips of the four thermocouples were placed in the silver bead to
improve thermal anchoring (Figure 6.24). The temperature data was collected using the

**Figure 6.24.** Arrangement of the T-type thermocouples on the surface of the hater block for characterization of the thermocouples.

**Figure 6.25.** Time required for the heater block temperature to stabilize with 15 V AC applied to the heater.

improve thermal anchoring (Figure 6.24). The temperature data was collected using the
National Instruments (NI) program *Temperature.vi* at a rate of 4 samples per second, 100 data points, and the average and standard deviation were calculated. The temperature was recorded periodically over 60 minutes. The time required for the heater block temperature to stabilize was investigated and a typical response of the various voltages is shown in Figure 6.25, when 15 V AC was applied to the heater element. It can be seen that a typical time for the temperature to stabilize was approximately 30 minutes, also that TC₄ falls outside the typical response of the thermocouples, and based on the standard deviation TC₁ and TC₂ are not significant different. The average stabilized temperature measured by the probes was 54.74 ± 0.50 °C when the heater voltage was 15 V AC.

To determine a reasonable temperature achievable by the heater blocks, voltage was applied to the heater element at approximate values of 0 (room temperature), 2.5, 5, 10, 15, 20 and 25 volts AC and the resultant temperature measured by the four probes

![Figure 6.26](image-url). The stabilized temperature recorded by the thermocouples at various heater voltages.
was recorded. The results are shown in Figure 6.26, and at a heater voltage of 25 V and average temperature of 100.55 ± 0.71 °C was achieved. Again, based on the standard deviation TC1 and TC2 are not significantly different, and exponential trend lines determined that the R² value for TC1 and TC2 were 0.9940 and 0.9941, respectively.

The efficacy of the apparatus enclosure to minimize temperature measurement errors was investigated. As an example, when the heater block was adjusted to 25 V and TC1 measured the temperature to be 99.18 ± 0.20 °C with the enclosure and 87.53 ± 2.05 °C without the enclosure in place.

Based on these results, using an apparatus enclosure assists in reducing and temperature fluctuations and radiative loses. This will lead to reduction in measurement errors that are reportedly problematic of Seebeck coefficient measurements. It was also determined that TC1 and TC2 were to be used to measure the temperature of the sample, \( T_H \) and \( T_L \), respectively, while the lesser accurate TC3 and TC4 were used to monitor the heater block and heat sink temperatures, respectively.

A random thin film sample on a quartz substrate was affixed in the apparatus and the average temperature of the sample was adjusted for trials at approximately 27, 63, and 95 °C. The temperature of heater block 1 was then adjusted to vary the temperature difference, \( \Delta T = T_H - T_L \), within 0 to 5 °C. As shown in Figure 6.27, at temperatures near ambient the deviation in temperature is lowest, approximately 0.28 °C, resulting in low deviation of the Seebeck voltage potential, \( \Delta V \). As the temperature is increased much greater than ambient, approximately 95 °C, the deviation of \( \Delta T \) and \( \Delta V \) is strongly significant. In order to minimize error, temperatures near ambient will be utilized in determination of the Seebeck coefficient utilizing this particular apparatus.
Figure 6.27. The voltage potential as a function of the temperature difference at various average temperatures.

Figure 6.28. The thermopower ($a_b$) of the Cu lead of the thermocouples used in the Seebeck apparatus.
The thermocouple lead contribution \( (a_b) \) to the thermopower (see equation 6.2) was determined by affixing a sample of the Cu lead wire to the Seebeck apparatus and measuring the resultant voltage potential as a function of the temperature differential and calculating the thermopower \( (a_b) \). The lead contribution must be known and subtracted from each data point at each temperature. The results are shown in Figure 6.28 and are consistent with references.

**Table 6.6.** The results of the room temperature thermopower measurements \( (S) \) and power factor \( (S^2/\rho) \) for thin films deposited by single and dual-laser ablation at various thicknesses \( (d) \). The resistivity determined by the Van der Pauw method (Table 6.2) are included for reference. \( p \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>PLD</th>
<th>Fluence ( (J/cm^2) )</th>
<th>( d ) ( (nm) )</th>
<th>( \rho ) ( (m\Omega \cdot cm) )</th>
<th>( S ) ( (\mu V/K) )</th>
<th>( S^2/\rho ) ( (\mu W/cm\cdot K^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single</td>
<td>3 UV</td>
<td>300</td>
<td>( 6.7 \times 10^4 )</td>
<td>-864</td>
<td>( 1.1 \times 10^2 )</td>
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<tr>
<td>2</td>
<td>Dual</td>
<td>1 UV + 2 IR</td>
<td>202</td>
<td>( 3.58 \times 10^3 )</td>
<td>-117</td>
<td>( 3.8 \times 10^3 )</td>
</tr>
<tr>
<td>3</td>
<td>Dual</td>
<td>1 UV + 2 IR</td>
<td>269</td>
<td>( 1.60 \times 10^3 )</td>
<td>-119</td>
<td>( 8.9 \times 10^3 )</td>
</tr>
<tr>
<td>4</td>
<td>Dual</td>
<td>1 UV + 2 IR</td>
<td>435</td>
<td>( 4.31 \times 10^2 )</td>
<td>-112</td>
<td>( 2.9 \times 10^2 )</td>
</tr>
<tr>
<td>5</td>
<td>Dual</td>
<td>1 UV + 2 IR</td>
<td>632</td>
<td>( 2.10 \times 10^1 )</td>
<td>-105</td>
<td>( 5.3 \times 10^1 )</td>
</tr>
</tbody>
</table>

**6.6. Summary**

In conclusion, this chapter described the topography, structure, and electrical transport properties of the thin films deposited by single and dual-laser ablation. The \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) material was found produce undesirable particulates and molten droplets, weak crystallinity, and excessively high resistivity when deposited by KrF single-laser ablation. These poor thin film characteristics were circumvented by the use the dual-laser ablation technique. Through proper coupling of the \( \text{CO}_2 \) laser energy with the excimer laser-generated plasma, control of particle reduction was demonstrated as well as high...
crystallinity. These characteristics lead to decreased film resistivity and desirable thermopower.

Thicker film depositions were performed to determine the effect on the electric transport properties. However, but due to the development of micro-cracks in the high fluence single laser thin-films with thickness greater than 300 nm, the resistivity increased due to discontinuity of the film. This was not the case with dual-laser deposited thin-films. High resistivity values may be due to vacancies on the framework sites [5]. Vacancies may introduce shallow defects near the conduction band, lowering the Hall mobility and thus increasing the resistivities as compared to Ba$_8$Ga$_{16}$Ge$_{30}$.

The resistivity ($\rho$, mΩ·cm) and majority carrier density ($n$) were determined using the van der Pauw – Hall method. The thermopower, or Seebeck coefficient ($S$, µV/K), was determined using a thermopower differential method with small $\Delta T$. These results, Table 6.4, were used to calculate the thermoelectric power factor, $P = S^2/\rho$ (µW/cm·K$^2$), for comparison. With increasing film thickness the resistivity decreased by approximately two orders of magnitude, assumed to be due to reduced surface interface effects. The carrier density increased from $10^{16}$ toward $10^{19}$ cm$^{-3}$, a range approaching the optimum value. The temperature gradient established for determination of the Seebeck coefficient is driven predominately by the thermal conductivity (1.3 W/m·K) and mass of the amorphous quartz substrate and film surface losses rather than the inherent characteristics of the Ba$_8$Ga$_{16}$Ge$_{30}$ clathrate material. Improvement of the power factor was shown with increasing film thickness, with a maximum room temperature power factor of 0.53 µW/cm·K$^2$ achieved which is comparable to reported values for the bulk material near room temperature.
CHAPTER 7:
CONCLUSIONS

The aim of this work was to grow thin films of the type-I clathrate Ba$_8$Ga$_{16}$Ge$_{30}$, for thermoelectric applications by pulsed laser ablation. Type-I clathrates exhibit a multi-component, complex structure composed of elements with a broad range of physical properties. These characteristics can be challenging parameters for thin-film deposition processes. Pulsed laser ablation/deposition is a technique which offers unique advantages for successful deposition of complex multicomponent materials such as Ba$_8$Ga$_{16}$Ge$_{30}$. Under the proper choice of laser fluence films have the same composition as the target. This sets PLD apart from incongruent-transfer methods such as thermal evaporation and sputtering.

The source material was polycrystalline type-I Ba$_8$Ga$_{16}$Ge$_{30}$ clathrate powder synthesized by the Novel Materials Laboratory at the Department of Physics, University of South Florida, under the supervision of Dr. George Nolas. The source material was cold-pressed into a packed-powder target for pulsed laser ablation. This work was divided into four main areas of study; (i) laser-target interaction to determine ablation parameters that are conducive to stoichiometric evaporation, (ii) in-situ optical diagnostics of the ablated material to investigate plume expansion dynamics, (iii) deposition of thin-films, and (iv) investigation of their properties.
Ablation from a stoichiometric target leading to stoichiometric evaporation of the target material, minimal ejection of particulates or droplets in the evaporated material plume, and congruent expansion of the ablated elemental components is desirable. The laser-target interaction studies involved impinging single-laser pulsed and dual-laser pulses on the target surface at various laser fluences and total laser pulses per target site. The surfaces of the ablated target regions were examined by scanning electron microscopy (SEM) to determine the morphological changes of the target. It was found that low fluence single-laser ablation, 1 J/cm^2, of the target developed conical structures that are about 50 µm wide, which is indicative non-stoichiometric evaporation of the material. High fluence single-laser ablation, 3 J/cm^2, resulted in a smooth laser-target melt zone which is conducive for stoichiometric evaporation. Preliminary studies found that single-laser ablation leads to varying degrees of particulate deposition while laser-target studies for the dual-laser ablation technique showed a smooth laser-target melt zone similar to 3 J/cm^2 single-laser ablation. Compositional analysis of the laser-target interaction sites by energy dispersive spectroscopy (EDS) found near-stoichiometric removal of material by the properly synchronized dual-laser ablation as well as for high fluence single-laser ablation. Ablation was not congruent for single laser deposition at fluences near 1 J/cm^2.

In-situ optical diagnostics was performed to investigate the ionic emission of the ablated material, expansion profiles of the barium, gallium, and germanium components, and to determine plasma temperatures of the various laser-ablation. The diagnostics involved visible wavelength optical emission spectroscopy (OES), two-dimensional ICCD imaging, time-gated imaging and time-of-flight spectroscopy. The dual-laser ablation was found to ionize the elemental components in the plume to a greater degree,
as compared to its single-laser component (1 J/cm²). The dual-laser ablation conditions produced broader expansion profiles and maintained congruent expansion profiles of the components. On the other hand, expansion profiles of components produced by the single laser ablation deviated from each other due to the small cone angle of expansion. A mathematical model of the plasma expansion was employed to determine the plasma temperature, with a comparison between single and dual-laser ablation. The low and high fluence single-laser ablation produced plasma temperatures of 7600 K and 14700 K, respectively. Dual-laser ablation plasma temperature was calculated to be 28400 K. The high plasma temperature was the dual-laser ablation characteristic which contributed to the high ionization, high velocity which leads to increased kinetic energy, and broader expansion profiles. These are all factors which are necessary for high-quality thin-film growth.

Thin films deposited were investigated by x-ray diffraction (XRD) to determination crystallinity, scanning electron microscopy (SEM) to analyze the surface morphology, energy dispersive spectroscopy (EDS) to determine the elemental composition. It was found that deposition by the dual-laser technique with modest laser energy densities produced thin-films with better structural properties such as increased crystallinity, minimal density of particulates, and stoichiometric depositions. High-energy single-laser depositions resulted in comparable crystallinity and stoichiometry, however, the particulate density on the films was unacceptable.

The electric transport properties of films deposited by excimer-only single-laser ablation had high resistivities which were beyond the instruments range. This was found to be due to micro-cracks which developed in the films, most probably due to the excessive strain in the deposited films. Dual-laser deposited films produced superior
electrical properties as compared to that if the single-laser deposited films. The room temperature electric transport properties such as the Seebeck coefficient and power factor ($\alpha^2\sigma$) were comparable to polycrystalline Ba$_8$Ga$_{16}$Ge$_{30}$ bulk values.
REFERENCES


[93] NIST Physics Laboratory, “Handbook for Basic Atomic Spectroscopic Data,”


APPENDICES
### Appendix A: Wyckoff Positions

**Table A.1.** The Wyckoff positions for the crystallographic cubic space group Pm-3n, applicable to the type-I clathrate Ba$_8$Ga$_{16}$Ge$_{30}$ [102].

<table>
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<th>Multiplicity</th>
<th>Wyckoff letter</th>
<th>Site Symmetry</th>
<th>Coordinates</th>
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Appendix B: Grit Designation Table

Table B.1. ISO grit designation and average grit diameter.

<table>
<thead>
<tr>
<th>Grit Size Table</th>
<th>ISO/FEPA Grit Designation</th>
<th>Average Particle Diameter (µm)</th>
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<tbody>
<tr>
<td><strong>MACROGRITS</strong></td>
<td></td>
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</tr>
<tr>
<td>Extra Coarse (Very fast removal of material)</td>
<td>P12</td>
<td>1815</td>
</tr>
<tr>
<td></td>
<td>P16</td>
<td>1324</td>
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<td>P30</td>
<td>642</td>
</tr>
<tr>
<td></td>
<td>P36</td>
<td>538</td>
</tr>
<tr>
<td>Coarse (Rapid removal of material)</td>
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<td>425</td>
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<td></td>
<td>P50</td>
<td>336</td>
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<tr>
<td>Medium (preparation for finishing, for gentle removal of varnish)</td>
<td>P60</td>
<td>269</td>
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<tr>
<td></td>
<td>P80</td>
<td>201</td>
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<tr>
<td>Fine (preparation for finishing, not suitable for removing varnish or paint, use for cleaning)</td>
<td>P100</td>
<td>162</td>
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<tr>
<td></td>
<td>P120</td>
<td>125</td>
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<tr>
<td>Very Fine (sanding of bare material)</td>
<td>P150</td>
<td>100</td>
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<td></td>
<td>P180</td>
<td>82</td>
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<td><strong>MICROGRITS</strong></td>
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<td>Very Fine (sanding finishes between coats)</td>
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<td>Super fine (final sanding of finishes)</td>
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<td>P2500</td>
<td>8.4</td>
</tr>
</tbody>
</table>
Appendix C: Properties of Ba$_8$Ga$_{16}$Ge$_{30}$ Target Components

Table C.1. Properties of the target components; barium, gallium, and germanium.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Barium</th>
<th>Gallium</th>
<th>Germanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td></td>
<td>Ba</td>
<td>Ga</td>
<td>Ge</td>
</tr>
<tr>
<td>Atomic Number</td>
<td></td>
<td>56</td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td></td>
<td>137.327</td>
<td>69.723</td>
<td>72.61</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm$^3$</td>
<td>3.62</td>
<td>5.91</td>
<td>5.32</td>
</tr>
<tr>
<td>Atomic Volume</td>
<td>cm$^3$/mol</td>
<td>39.24</td>
<td>11.8</td>
<td>13.6</td>
</tr>
<tr>
<td>Covalent Radius</td>
<td>Å</td>
<td>1.98</td>
<td>1.26</td>
<td>1.22</td>
</tr>
<tr>
<td>Atomic Radius</td>
<td>Å</td>
<td>2.78</td>
<td>1.81</td>
<td>1.52</td>
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<tr>
<td>Oxidation States</td>
<td></td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Electron Configuration</td>
<td></td>
<td>(Xe)6s$^2$</td>
<td>(Ar)3d$^{10}$4s$^2$4p$^1$</td>
<td>(Ar)3d$^{10}$4s$^2$4p$^2$</td>
</tr>
<tr>
<td>Melting Point</td>
<td>°C</td>
<td>727</td>
<td>29.8</td>
<td>937.2</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>°C</td>
<td>1640</td>
<td>2403</td>
<td>2830</td>
</tr>
<tr>
<td>Acid-Base Properties</td>
<td></td>
<td>basic</td>
<td>weak amphoteric</td>
<td>weak amphoteric</td>
</tr>
<tr>
<td>Thermal Conductivity (300K)</td>
<td>[W/(cm·K)]</td>
<td>0.184</td>
<td>0.406</td>
<td>0.599</td>
</tr>
<tr>
<td>Specific Heat (300K)</td>
<td>J/(g·K)</td>
<td>0.204</td>
<td>0.37</td>
<td>0.32</td>
</tr>
<tr>
<td>Heat of Fusion (melting pt.)</td>
<td>kJ/mol</td>
<td>7.750</td>
<td>5.590</td>
<td>36.940</td>
</tr>
<tr>
<td>Heat of Vaporization (boiling pt.)</td>
<td>kJ/mol</td>
<td>142.0</td>
<td>258.70</td>
<td>330.90</td>
</tr>
<tr>
<td>Latent Heat of Fusion</td>
<td>k-cal/g·atom</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Latent Heat of Vaporization</td>
<td>cal/g</td>
<td></td>
<td></td>
<td>1100</td>
</tr>
<tr>
<td>First Ionization Potential (300K)</td>
<td>V</td>
<td>5.212</td>
<td>5.999</td>
<td>7.899</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>Pauling’s</td>
<td>0.9</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>microOhms·cm</td>
<td>50</td>
<td>53.4</td>
<td>47 (27°C)</td>
</tr>
<tr>
<td>Electrical Conductivity (293K)</td>
<td>10$^6$/(Ω·cm)</td>
<td>0.030</td>
<td>0.0678</td>
<td>1.45x10$^4$</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td></td>
<td>bcc</td>
<td>Orthorhombic</td>
<td>Diamond</td>
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<tr>
<td>Work Function</td>
<td>eV</td>
<td>2.5</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>mm Hg</td>
<td>760 (2400°C)</td>
<td>760 (27°C)</td>
<td></td>
</tr>
<tr>
<td>Vapor Pressure Temp. (10$^{-6}$ Torr)</td>
<td>°C</td>
<td>350</td>
<td>740</td>
<td>945</td>
</tr>
<tr>
<td>Cubic Coefficient of Expansion</td>
<td>K$^{-1}$</td>
<td>5.4x10$^{-6}$ (20°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear Coefficient of Expansion</td>
<td>K$^{-1}$</td>
<td></td>
<td></td>
<td>6.1x10$^{-8}$</td>
</tr>
<tr>
<td>Mohs Hardness</td>
<td></td>
<td>1.5-2.5 (20°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetic Susceptibility</td>
<td>emu/mole</td>
<td></td>
<td>-22x10$^6$ (20°C)</td>
<td></td>
</tr>
<tr>
<td>Debye Temperature</td>
<td>K</td>
<td></td>
<td>362</td>
<td></td>
</tr>
</tbody>
</table>

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Appendix D: ICCD Camera System Specifications

PI Acton PI-MAX:512 UNIGEN Digital ICCD Camera System:
Manufacturer: Princeton Instruments Acton
Model: 7361-0017
Serial Number: 2911060001
Thompson TH7895M scientific grade 1, front-illuminated CCD, 512 x 512 pixels
1.27:1 fiber-optic bonded 18 mm grade 1, Gen III extended blue image intensifier
   ideal for 350 nm to 900 nm range.
Fiber-optic input, proprietary UV coating
19 x 19 µm pixels (12.4 x 12.4 mm image area)
< 5 ns gating capable

ICCD USB2 Controller:
with 16-bit 100 kHz and 16-bit 1 Mhz digitizers
ST-133 B/U-PTG-Dual Model 7513-0001
Serial Number: 2911060002

Programmable Timing Generator (PTG):
Delay Range: ~0 ns to 20 ms
Timing Resolution: 40 ps
Timing Jitter: 40 ps rms
Repetition Rate: 50 kHz sustained; 500 kHz burst
Gate Width: 5 ns to 10 ms; 40 ps resolution
Fast Gate: 2 ns; 5 kHz repetition rate
Bracket Pulse: 5 kHz repetition rate; 500 ns lead time
Insertion Delay: 15 ns
Appendix E: Spectrometer Specifications

**Manufacturer:** Acton Research Corporation

**Model:** 1237 SpectraPro-500

**Serial Number:** 500173S

**Controller Serial Number:** 100-240V 2A

**Focal Length:** 500 mm

**Optical System:** Czerny-Turner type with in-line (180°) optical path, and optical multi-port configuration featuring 90° and 180° optical path.

**Wavelength Scanning System:** Direct Digital Scanning with exclusive AutoTrack™ electronics.

**Scan Linearity:** Scans linear with respect to wavelength.

**Triple Indexable Gratings:** 150, 600, and 1200 grooves/mm.

**Wavelength Display:** Automatically displays correct wavelength for gratings installed. Displays grating position, groove spacing and blaze wavelength for gratings.

**Resolution:** 0.05 nm with standard 1200 g/mm grating, 10 μm wide x 4 mm high slits, measured at 435.8 nm.

**Reciprocal Linear Dispersion:** 1.67 nm/mm with 1200 g/mm grating (nominal).

**Aperture Ratio:** f/6.9

**Wavelength Operating Range:** Up to the far infrared with available gratings. 185 nm to 1.4 μm with 1200 g/mm grating.

**Wavelength Accuracy:** ± 0.2 nm/500 nm with a 1200 g/mm grating.

**Wavelength Reproducibility:** ± 0.5 nm with 1200 g/mm.

**Focal Plane Detector Compatibility:** 25 mm focal plane extends 0.750 inch (19 mm) beyond housing for easy positioning of focal plane detectors. Provides nominal 280 nm coverage with 150 g/mm grating, 140 nm with 300 g/mm grating, 70 nm with 600 g/mm grating, and 35 nm with 1200 g/mm grating.
Slits: Standard slits are bilaterally adjustable from 10 μm to 3.0 mm, via external micrometer. Standard slit height is 4 mm. Other slit heights up to 20 mm can be supplied.

**Computer Compatibility:** RS-232 port – 9600 baud, no parity, 8 data bits, 1 start bit, 1 stop bit; or optional IEEE 48 port.

![Spectrograph optical layout](image)

**Figure E.1:** Spectrograph optical layout.
Appendix F: Fiber Optic Bundles

Standard bundles come with 200 µm diameter fibers in silica for UV-VIS. Fibers are arranged as a slit pattern (in a 10 mm diameter ferrule) on the spectrograph end, with a round configuration (in SMA 905 connectors) on the source end.

Two-Leg Fiber Bundle
Model BFB-455-7: a 1 m long UV VIS fiberoptic bundle for 190 to 1100 nm. It contains two groups of 200 µm diameter fibers (~245 micron diameter with cladding), with seven fibers per group and ~1 mm spacing between groups.

Four-Leg Fiber Bundle
Model QFB-455-3: a 1 m long UV_VIS fiberoptic bundle for 190 to 1100 nm. It contains four groups of 200 µm diameter fibers (~245 micron diameter with cladding), with three fibers per group and ~1 mm spacing between groups.

![Figure F.1](image-url) 10 mm diameter ferrule on spectrograph end for (a) two-leg fiber bundle and (b) four-leg fiber bundle.
Figure F.2. The three fiber configuration on the source end of the four-leg fiber bundle. An approximate 528 µm diameter fiber bundle zone (including cladding), an approximate 483 µm diameter light collection zone (not including cladding at outer edge).
Appendix G: OES and ICCD Procedure

Imaging

Data Collection

Data Analysis
Following is the procedure to extract the desired Region of Interest (ROI) (ex.: Fiber Bundle Leg 3) from the collected WinSpec Glue Files, and then convert the resulting ROI files to Text ASCII files for further analysis in a spreadsheet program such as Microsoft Excel.

Create the following folders:
- Step Files
- Original Glue Files
- Excel Files
- ROI Leg 3 with 2 sub folders of Text Files and WinSpec Files

Sort the Step Files and the Original Glue Files into their respective folders.

Start the WinSpec/32 program. When using the program without the spectrometer and camera, a warning window will appear Camera not found..., click Cancel and a warning Error Communicating With Acton SP500 on Com1, click Cancel.

Under the Process menu select Binning and Skipping
Under the Input tab:
- Select the Input Image (*.SPE file) from the Original Glue Files
- Frame is set at 1 to 1
- X Range is set at 1 to 1294
- Y Range is set at 271 to 310 from Leg 3

Following are the Regions of Interest (ROI) for each leg of the four-leg fiber bundle:
- 126 to 165 for Leg 1
- 199 to 238 for Leg 2
- 271 to 310 for Leg 3
- 342 to 381 for Leg 4

Datatype is shown as FLOAT, this parameter is set later

Under the Parameters tab:
- Binning is set at X Dimension 1 and Y Dimension, Average is not selected
- Under Skipping, X Dimension is set at 0 and Y Dimension is set at 0

Under the Output tab:
- for Output Image type the filename (usually the Input Image filename with 3 added to the end * 3.SPE) in folder ROI Leg 3
- Display Result is selected
Datatype is set at FLOAT
Click Apply button, the resulting region of interest (ROI) is displayed.
Repeat the procedure for the remaining files. The previous settings remain except for Y Range.

To convert the ROI WinSpec Files to Text files:
In the WinSpec/32 program under the Tools menu select Convert to ASCII
In the .SPE To ASCII Conversion window:
  Click the Choose Files button, select all the (* 3.SPE) files from the WinSpec Files folder, all the filenames selected will be displayed in the File Name window
  Click the Choose Output Directory button and select the Text Files folder under the ROI Leg 3 folder
  Frame No.: set at 1 to 512
  File Extension: set to txt
  Delimiter set to Tab
  X-Axis set to nm
  Output Order set to Pixel, Intensity
  New Line Characters select both Carriage Return and Line Feed
  Output File Options select One File for all Frames and Single Column
  Pixel Format select Preserve CCD X/Y/Frame Dimension Value
  Click Convert to ASCII button. While the conversion is being performed, the Convert to ASCII button is dimmed, and depending on the number file files being converted and the destination, each file takes approximately 1 second to convert.
  Click the Done button when finished.

Exit the WinSpec program.
Appendix H: Hydrodynamic Plasma Model Maple Program

The plasma model was computed using Maple 9.50. Distances are entered as centimeters (cm) and time as microseconds (\(\mu\)s). The program, Plasma Model.mw, is as follows with Maple code (red print), and sample input data (blue print).

```maple
> restart;
>
> # Input Parameters
> Sh := 1.0; # laser spot horizontal dimension from center (mm)

\[
Sh := 1.0
\]

> Sv := 1.5; # laser spot vertical dimension from center (mm)

\[
Sv := 1.5
\]

> Pt := 22.5; # plasma thickness (micrometer)

\[
Pt := 22.5
\]

> Temp := 8000; # plasma temperature (K)

\[
Temp := 8000
\]

> aw := 81.33; # atomic weight

\[
aw := 81.33
\]

> vx := 0.6335; # initial x-velocity (m/s)

\[
vx := 0.6335
\]

> vy := 0.1901; # initial y-velocity (m/s)

\[
vy := 0.1901
\]

> vz := 0.1267; # initial z-velocity (m/s)

\[
vz := 0.1267
\]

> tid := 0; # initial delay time (ns)

\[
tid := 0
\]

> tstart := 0; # start time (ns)

\[
tstart := 0
\]

> tend := 2000; # end time (ns)
```

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\[
\begin{align*}
tend & := 2000 \\
tgate & := 20; \quad \text{# gate time (ns)} \\
gama & := 1.6; \quad \text{# exponent factor} \\
xd & := 6; \quad \text{# on-axis distance for TOF (mm)}
\end{align*}
\]

\[
\begin{align*}
\text{Digits} & := 5; \quad \text{# number of digits used for calculations} \\
\text{# Conversions Constants and Calculations} \\
a & := Pt/(1*10^6); \quad \text{# plasma thickness unit conversion (m)} \\
b & := Sh/(1*10^3); \quad \text{# laser spot horizontal dimension unit conversion (m)} \\
c & := Sv/(1*10^3); \quad \text{# laser spot vertical dimension unit conversion (m)} \\
ti & := tid/(1*10^9); \quad \text{# initial delay time unit conversion (sec)} \\
ts & := tstart/(1*10^9); \quad \text{# start time unit conversion (sec)} \\
tf & := tend/(1*10^9); \quad \text{# end time unit conversion (sec)} \\
DT & := tgate/(1*10^9); \quad \text{# gate time step unit conversion (sec)} \\
d & := xd/(1*10^3); \quad \text{# on-axis distance unit conversion (m)} \\
k & := 1.3810*10^{-23}; \quad \text{# Boltzmann constant (J/K)} \\
eV & := 1.60210*10^{(-19)}; \quad \text{# Joules to eV conversion (eV)} \\
u & := 1.661*10^{(-27)}; \quad \text{# unified atomic mass unit (kg)} \\
Const & := (6*k*Temp)/(aw*u); \quad \text{# constant} \\
Const & := 4.9069 \times 10^6 \\
\text{with(DEtools):} \\
\text{eqns} & := \\
\text{diff(x(t),t$2)*x(t)=Const*((a*b*c)/(x(t)*y(t)*z(t)))^(gama-1),} \\
\text{diff(y(t),t$2)*y(t)=Const*((a*b*c)/(x(t)*y(t)*z(t)))^(gama-1),} \\
\text{diff(z(t),t$2)*z(t)=Const*((a*b*c)/(x(t)*y(t)*z(t)))^(gama-1);} \\
\text{# plasma expansion equations}
\end{align*}
\]

\[
\begin{align*}
eqns & := \begin{pmatrix}
\frac{d^2}{dt^2} x(t) \\
\frac{d^2}{dt^2} y(t) \\
\frac{d^2}{dt^2} z(t)
\end{pmatrix} \\
& = 2.5572 \begin{pmatrix}
\frac{1}{x(t)} \frac{1}{y(t)} \frac{1}{z(t)}^0.6 \\
\frac{1}{x(t)} \frac{1}{y(t)} \frac{1}{z(t)}^0.6 \\
\frac{1}{x(t)} \frac{1}{y(t)} \frac{1}{z(t)}^0.6
\end{pmatrix}
\end{align*}
\]
> initvals := x(ti)=a, y(ti)=b, z(ti)=c, D(x)(ti)=vx, 
D(y)(ti)=vy, D(z)(ti)=vz: # initial conditions for position 
and velocity

> L := dsolve({eqns, initvals}, {x(t), y(t), z(t)}, 
type=numeric, output=listprocedure); # solve ordinary 
differential equation with initial conditions

\[
\begin{align*}
L := & [t = \text{proc}(t) \ldots \text{end proc}, x(t) = \text{proc}(t) \ldots \text{end proc}, \frac{d}{dt} x(t) = \text{proc}(t) \ldots \text{end proc}, \\
& y(t) = \text{proc}(t) \ldots \text{end proc}, \frac{d}{dt} y(t) = \text{proc}(t) \ldots \text{end proc}, z(t) = \text{proc}(t) \ldots \text{end proc}, \\
& \frac{d}{dt} z(t) = \text{proc}(t) \ldots \text{end proc}];
\end{align*}
\]

> T := rhs(L[1]): # time
> X := rhs(L[2]): # x-position
> X1 := rhs(L[3]): # x-velocity
> Y := rhs(L[4]): # y-position
> Y1 := rhs(L[5]): # y-velocity
> Z := rhs(L[6]): # z-position
> Z1 := rhs(L[7]): # z-velocity
> FLX := t->((X(t)^2*Y(t)*Z(t))^(-1))*d*X1(t)*exp(-
(d^2/(2*(X(t)^2)))); # flux

\[
\begin{align*}
\text{FLX} := & t \to \left(\frac{d^2}{2 X(t)^2}\right) X(t)^2 Y(t) Z(t)
\end{align*}
\]

> TOF := t->FLX(t)*DT; # time of flight

\[
\begin{align*}
\text{TOF} := & t \to \text{FLX}(t) DT
\end{align*}
\]

> for t from ts by DT to tf do TOF(t) end do;

1.6822 × 10^{-15437}
1.1677 × 10^{-2593}
2.0780 × 10^{-596}
1.0963 × 10^{-234}
1.9759 × 10^{-119}
4.5118 × 10^{-70}
Appendix I: PLD Procedure

- **Substrate Preparation**
  - Standard clean
    - Cut substrate, typical substrate size is $\frac{1}{2} \times \frac{1}{2}$ inch square
    - Sonic bath in acetone 15 minutes
    - Sonic bath in methanol 15 minutes
    - De-ionized water rinse
    - Blow dry with nitrogen gas
  - Mount substrate
    - Adhere with conductive silver paint
    - Cover edge strip with stainless steel step mask for thickness measurement
    - Dry silver paint by pre-heating heater block and substrate to approximately 100 °C for 20 minutes, then allow to cool to touch
  - Mount substrate holder/ heater block
    - Secure the substrate holder at the predetermined target-substrate distance
    - Center the substrate on-axis with the target-laser spot center
    - Rotate the substrate shield to block the plume from the substrate
  - Check bulb heater and thermocouple connections

- **Chamber Preparation**
  - Clean laser windows
    - Polish laser windows with optical polishing powder
    - Rinse with water
    - Blow dry with nitrogen gas
    - Wipe Viton o-ring and o-ring groove with methanol
    - Reseat window
    - Wipe chamber inside walls with acetone followed with methanol
    - Wipe chamber lid o-ring with methanol and reseat o-ring

- **Laser Preparation**
  - Turn on the laser(s)
    - Adjust laser energy to achieve the predetermined laser fluence
    - Adjust the laser focusing lens for proper laser spot size and position

- **Evacuate Chamber**
  - Close chamber lid
  - Close pressure relief valve
  - Turn on roughing pump
  - Open gate valve
  - Open cryo-pump gate valve, if the pump is to be employed
o Pump chamber until pressure is less than 200 milli-torr, typically requires 3 minutes or less
o Turn on turbo molecular pump
o Turn on substrate heater to assist in de-gassing and baking-out the chamber
  o Evacuate chamber to less than $1 \times 10^{-5}$ torr
  o If needed, close cryo-pump gate valve, turn on cryo-pump
  o Evacuate chamber to $1 \times 10^{-6}$ torr or less
  o If needed, close the roughing/turbo pump gate valve, the pressure should drop to low $10^{-7}$ torr

- **Deposition**
  o When the chamber pressure is in the $10^{-6}$ torr range, raise the substrate heater temperature to the desired temperature
  o Allow the temperature to stabilize for at least 20 minutes
  o Start the target rotation
  o Turn on laser(s)
  o Laser-condition the target surface
  o Rotate the substrate shield from in front of the substrate
  o Reset the laser pulse counter
  o Start the laser ablation for the predetermined number of pulses
  o Stop laser pulses

- **Substrate Cool-Down**
  o Five minutes after the deposition was completed, reduce the heater voltage by 1 volt AC every 2.5 minutes until 0 volts is reached. Sample cool-down rate is shown in Figure M.1.
  o Allow the heater block to continue to cool to approximately room temperature
Figure I.1. Substrate heater cool-down time from 300 °C to room temperature with 1 V AC reduction every 2.5 minutes until 0 V AC is reached.
Appendix J: Electron Binding Energies

Table J.1. The electron binding energy for oxygen (O), silicon (Si), gallium (Ga), germanium (Ge), strontium (Sr), and barium (Ba).

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>8</th>
<th>14</th>
<th>31</th>
<th>32</th>
<th>38</th>
<th>56</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>O</td>
<td>Si</td>
<td>Ga</td>
<td>Ge</td>
<td>Sr</td>
<td>Ba</td>
</tr>
<tr>
<td>Orbital</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1s</td>
<td>0.543</td>
<td>1.839</td>
<td>10.367</td>
<td>11.103</td>
<td>16.105</td>
</tr>
<tr>
<td>L-I</td>
<td>2s</td>
<td>0.042</td>
<td>0.150</td>
<td>1.299</td>
<td>1.415</td>
<td>2.216</td>
</tr>
<tr>
<td>L-II</td>
<td>2p1/2</td>
<td>0.100</td>
<td>1.143</td>
<td>1.248</td>
<td>2.007</td>
<td>5.624</td>
</tr>
<tr>
<td>L-III</td>
<td>2p3/2</td>
<td>0.099</td>
<td>1.116</td>
<td>1.217</td>
<td>1.94</td>
<td>5.247</td>
</tr>
<tr>
<td>M-I</td>
<td>3s</td>
<td>0.160</td>
<td>0.180</td>
<td>0.3587</td>
<td>1.293</td>
<td></td>
</tr>
<tr>
<td>M-II</td>
<td>3p1/2</td>
<td>0.104</td>
<td>0.125</td>
<td>0.2803</td>
<td>1.137</td>
<td></td>
</tr>
<tr>
<td>M-III</td>
<td>3p3/2</td>
<td>0.100</td>
<td>0.121</td>
<td>0.27</td>
<td>1.063</td>
<td></td>
</tr>
<tr>
<td>M-IV</td>
<td>3d3/2</td>
<td>0.019</td>
<td>0.030</td>
<td>0.136</td>
<td>0.796</td>
<td></td>
</tr>
<tr>
<td>M-V</td>
<td>3d5/2</td>
<td>0.019</td>
<td>0.029</td>
<td>0.1342</td>
<td>0.781</td>
<td></td>
</tr>
<tr>
<td>N-I</td>
<td>4s</td>
<td>0.0389</td>
<td>0.254</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>4p1/2</td>
<td>0.0216</td>
<td>0.192</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-III</td>
<td>4p3/2</td>
<td>0.0201</td>
<td>0.179</td>
<td></td>
<td></td>
<td></td>
</tr>
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The energies are given relative to the vacuum level for rare gases and H, N, O, F, and Cl diatomic molecules; relative to the Fermi level for metals; and relative to the top of the valence band for semiconductors. Values are taken from [103-105].
Table K.1. The output energy and delay for the CO\textsubscript{2} laser germanium output couplers.

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<th>Curvature (m)</th>
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Appendix L: Publications and Presentations

Appendix L.1. Journal Publications


Appendix L.2. Published Conference Proceedings


Appendix L.3. Conference Presentations - Presentations


Appendix L.4. Conference Presentations - Poster Presentations


“Growth of Epitaxial CoFe$_2$O$_4$/PZT Heterostructures and Ferroelectric Characterization” *University of South Florida Poster Symposium & Competition, Tampa FL*(2008).


ABOUT THE AUTHOR

Robert H. Hyde received his Bachelor’s of Science degree in Physics from Lock Haven University of Pennsylvania in 1991. Prior to attending the University of South Florida, he was employed in Research & Development with Wardley Corp./Hartz Maountain, leading to co-inventor of three U.S. Patents. He completed the Dual Master’s of Science program in Engineering Science and Physics from the University of South Florida in 2006 and entered the Applied Physics Ph.D. program in 2007. He has been awarded the University of South Florida Graduate Research Symposium Award, Frank E. Duckwall Graduate Fellowship, and Fred L. & Helen M. Tharp Endowment Scholarship during the course of his graduate work. The research conducted during his graduate tenure at USF resulted in presentations at conferences and symposiums, multiple poster and oral presentations. This work also lead to five published conferences proceedings and two peer reviewed journal publications.