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Maskless Patterning on CVD Diamond Films by Excimer Laser

By

Jong-kook Park

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

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Extensive investigations were conducted in this study to examine the excimer laser ablation process for maskless patterning on chemical vapor deposition (CVD) This study has two major topics: (i) macroscopic and microscopic diamond films. analysis of laser-diamond coupling, and (ii) nature of the laser-induced plasma evolution. These two topics are closely linked to practical fabrication of patterned diamond components by the innovative maskless patterning techniques. The laser-diamond interaction is examined under various gas processing environments. The ablation rate of the CVD diamond film is measured, and linear and nonlinear models for the ablation process are developed. The initial stage of the laser-diamond interaction is observed by the atomic force microscope (AFM) and Raman spectroscope. To examine the development of the surface morphology, *in-situ* observation is performed by environmental scanning electron microscope (ESEM). Laser-induced plasma on the CVD diamond film is investigated by analytic instrumentations, such as laser-induced breakdown spectroscopy (LIBS), and time-integrated plasma image capturing. The excitation temperatures of the plasma are deduced by the Boltzmann-plot method. Electron densities are calculated from the proportionality between the Stark effect on the line broadening and the electron population. A maskless patterning system has been designed and demonstrated patterning on the diamond films. The results of this investigation establish the great potential of CVD diamond films for various applications, such as semiconductor devices, sensors, optical windows and microelectromechanical systems (MEMS).

To my wife and family

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscope
CCD	
CNC	Computer Numerical Control
СТЕ	Coefficient of Thermal Expansion
CVD	Chemical Vapor Deposition
ESEM	Environmental Scanning Electron Microscope
FWHM	Full Width Half Maximum
HELP	High Energy Laser Processing
LIBS	Laser Induced Breakdown Spectroscopy
LSM	Laser Scanning Microscope
LTE	Local Thermodynamic Equilibrium
MCPR7	
MEMS	Microelectromechanical Systems
NA	Numerical Aperture
NIST	National Institute of Standard and Technology
PAZ	Plasma Affected Zone
PPS	Pulse Per Second
SEM	Scanning Electron Microscopy
TEA	Transversely Excited Atmospheric Pressure
TEM	Transverse Electromagnetic Mode

Chapter I

INTRODUCTION

Rapidly growing demands on electronic materials seek high performance films. CVD diamond films inherit superior mechanical properties of a natural diamond, such as high hardness and moduli, wear resistance, and low friction coefficient. Also, potential of diamond films for electronic devices has been widely recognized by virtue of their largest intrinsic band gap, lowest dielectric constant, predicted high carrier mobility, high break down fields and thermal conductivity [1-6].

The excellent mechanical and electrical properties make chemical vapor deposited (CVD) diamond films uniquely qualified for the applications, such as integrated circuits, sensors, optical windows and microelectromechanical systems (MEMS) [7-10]. To utilize the excellent properties of the diamond films in the applications, micromachining and patterning of diamond films are primarily required [11, 12]. For ultra-hard film materials, such as CVD diamond, conventional machining and lithography-based patterning are difficult due to the high wear resistance and the chemical inertness. Pulsed laser ablation has been used for vaporizing film materials to make patterned structures and micro-components. The laser ablation is a direct process that requires only proper arrangement of optics to control the laser beam [13]. By subjecting a film surface to pulsed laser irradiation, a thin layer of the target surface is instantaneously ablated, creating micro patterns and/or structures on the surface. CVD diamond films have been processed by various types of pulsed lasers for this purpose [14-24]. Nanosecond-pulsed,

excimer lasers have been applied for surface modifications of CVD diamond films [14-16, 18-20]. In these investigations, the excimer lasers have shown their capabilities in polishing, etching, and patterning of the diamond films. Reduced surface roughness, improved optical transmittance, and patterned structures were reported from these applications. However, the processes have exhibited damage, such as transformed surface layers, and spoiled spot edges. These drawbacks have been obstacles to the application of the nanosecond-pulsed excimer lasers to high-resolution micromachining. Recently, femtosecond pulsed UV lasers have been introduced to overcome the drawbacks [21-24]. By utilizing the ultrashort-pulsed irradiation on the CVD diamond films, the ablation process could show some improvements as compared to that of the nanosecond pulsed laser process. Even though the ultrashort laser ablation showed improvements on surface finish and purity of the irradiated diamond films, it was not completely successful to avoid the damage, such as rippled surfaces, and blurred interfaces.

In the ablation processes, plasma formation is inevitable due to the characteristics of short or ultrashort pulsed laser irradiation. Even though the pulsed laser-material interaction is limited to nanoseconds to femtoseconds ranges, the plasma extends for far longer times than the laser pulse duration. In studies of ultrafast imaging of nanosecond pulsed laser ablation [13, 25-28], it was visualized that the formation and expansion of plasma, induced by ablative material ejection, extended up to tens of microseconds. Propagation of shock waves was also observed due to the expansion of the high temperature plasma, which exists long enough to transfer heat to the target surface. In these respects, the formation and expansion of the plasma give rise to the damage, such as plasma material ejection and deposition, spoiled interface, recast layers, and rippled surfaces. The plasma-induced damage has been an obstruction to achieve high-resolution micromachining and patterning of diamond films.

The high-resolution micromachining and patterning can be achieved by maximized acquisition of accuracy and controllability of the laser ablation process. The accuracy and controllability are directly related to plasma-diamond interaction and laserdiamond coupling, respectively. This study aims to investigate plasma-diamond interaction and laser-diamond coupling to improve the practical aspects of micromachining and patterning. The study of plasma-diamond interaction is mainly focused on novel approaches to minimize the plasma-induced damage. In this study, CVD diamond films were subject to various gas processing environments, such as ambient air, vacuum and gas-steaming condition. Evolution of plasma was significantly affected by these conditions, which alter the ionization potential of the processing environment. Various instrumentations, including the time-integrated plasma image capturing and the laser-induced breakdown spectroscopy (LIBS) were performed to analyze the laser-induced plasma. Observed damage were dependant on behavior of the plasma in the different processing environments. The dynamic gas-streaming proved that proper dissipation of the plasma led to precisely irradiated surfaces, which were almost free from damage. Emphases of the plasma study are to achieve maximum dissipation of the plasma and proper quenching of the target surface.

Laser-diamond coupling was investigated by macroscopic and microscopic analyses to characterize intrinsic properties of CVD diamond films. Most of the polycrystalline diamond films retain high surface roughness due to the nature of CVD

3

processing. In the microscopic analyses of the initial laser-diamond coupling, an atomic force microscope (AFM) was used to examine the subjected diamond films. Macroscopic changes of the surface morphologies were also examined by the *in-situ* observation upon the laser irradiation. The ablation rate of the CVD diamond film was measured to model the laser ablation process on the CVD diamond film.

For the laser ablation process of diamond films, applied and fundamental investigations are required to overcome the current barriers. Subsequently, maximum accuracy and controllability of the ablation process can produce the precisely micromachined, and patterned diamond films. In these respects, this study aims for two major goals; i) macroscopic and microscopic analysis of laser-diamond coupling, and ii) analysis on the laser-induced plasma and its interaction to surrounding. The fundamental aspects in this study were linked to practical fabrication of patterned diamond components by the innovative maskless patterning technique. The maskless patterning technique employs pulsed irradiation of focused laser beam on a target material, which is translated to the programmed positions by the micro-CNC. Along with its advantages of a simple setup and a direct process, the maskless process makes a rapid prototyping possible for patterns on ultra-hard film materials. The maskless patterning introduces CVD diamond films to new area of sensors, optical windows, integrated circuits and MEMS, where extreme tolerance of a material is required. Diamond films of unmatched materials properties will drastically increase performance in various potential applications.

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Chapter II

A BRIEF REVIEW OF LASERS AND CVD DIAMOND FILMS

2.1. Lasers

Lasers are extensively utilized in advanced materials processing. Therefore, an understanding of the basic laser principles, and their operation is essential for selecting right types of lasers for the related materials processing. In this section, basic principles of laser operation, and related types of lasers are briefly reviewed.

2.1.1. Fundamentals of lasers

The word *laser* stands for *light amplification by stimulated emission of radiation*. Laser makes use of processes that amplify light signals. Three fundamental phenomena such as absorption, spontaneous emission, and stimulated emission are related to the light amplification [29, 30].

Consider an atom with two energy levels, an upper level E_2 , and a lower level E_1 , as shown in Figure 1. The atom is initially lying in the lower level E_1 in ground state. When this atom is irradiated by an incident radiation with photon energy equal to or larger than the energy difference of the two levels $(E_2 - E_1)$, the atom is excited to the upper level E_2 . This is the energy absorption process. When the atom returns form E_2 to the ground state E_1 , the atom releases its excess energy by a radiative process; giving rise to spontaneous emission.



Figure 1. Schematic illustration for lasing mechanism, absorption, spontaneous emission and stimulated emission [31].

Spontaneous emission occurs when the excited atom spontaneously returns to the ground state by releasing the corresponding energy difference hv. It can be expressed by the relationship [29, 30]:

$$E_2 - E_1 = hv$$
 Equation 1

where h is Plank's constant, and v is frequency. Stimulated emission occurs when photons from the spontaneous emission trigger atoms in the excited state to emit radiation. Such stimulated emission has the monochromatic wavelength. This stimulated emission is constructively amplified to produce the laser beam. The light amplification is done by optical feedback, in which a set of mirrors feed the light back into the amplifier for continued growth of the developing laser beam.

<u>2.1.1-a. Lasing mechanism</u>

A laser is an optical transducer that converts input energy to intensively ordered light emission. The laser amplifies light and produces a highly directional beam that typically has a monochromatic wavelength. The laser consists of three major parts, an energy source for pumping, a lasing medium, and an optical resonator [29, 32].

In Figure 1, the population of atoms in the energy states E_1 and E_2 can be expressed by n_1 and n_2 , respectively. For a system in thermal equilibrium, the ratio of populations is given by the Boltzmann relationship [29, 30]:

$$\frac{n_2}{n_1} = \exp\left(\frac{E_1 - E_2}{kT}\right)$$
 Equation 2

where k is Boltzmann constant, and T is the absolute temperature of the material. According to the Boltzmann equilibrium, a larger population exists in a lower energy state, that is, $n_1 > n_2$. The population inversion is the nonequilibrium state where the population of higher energy state is greater than that of the lower energy state, that is $n_2 >$ n_1 . The population inversion is the basic requirement for lasing mechanism. The lasing occurs when the achieved population inversion is high enough to overcome energy losses inside the resonator. An external energy source is needed to buildup a population of atoms or molecules in excited states. This is called the 'pumping.' Optical pumping and electrical pumping are the basic pumping methods for lasers. Generally, gas lasers use electrical discharge, and solid-state lasers, such as Nd:YAG and ruby lasers, use the energy of flash lamps. For the optical pumping, continuous lasers use arc lamps and tungsten lamps, while pulsed lasers usually use flash lamps.



Figure 2. Schematic illustration for the light amplification in an optical resonator [29, 33].

2.1.1-b. Light amplification in optical resonator

A schematic illustration for the typical optical resonator is shown in Figure 2. The optical resonator contains a lasing medium, which is closed off with two mirrors, one is fully reflecting and the other is partially reflecting. The lasing medium is usually a crystal or rod for solid lasers, and long gas-containing tube for gas lasers. When an optically or electronically pumped lasing medium emits photons by spontaneous emission, these emitted photons stimulate emission from other excited atoms or molecules in the lasing medium. The stimulated emission, which occurs in the axis between the two mirrors, is amplified by multiple passages of photons through the medium. In this condition, photons are optically resonating in the cavity for the amplification. A laser beam is generated from the optical resonator when the amplification of resonating photons reaches enough intensity to overcome the threshold of the partially transmitting mirror [29, 30, 32, 33].

2.1.2. Characteristics of laser beam

2.1.2-a. Spatial pattern of laser beam

Transverse and longitudinal modes are the two distinct types of beam modes for the optical resonators [29, 34, 35]. Transverse modes describe the cross-sectional profile of the beam, and longitudinal modes correspond to different resonance along the length of the optical resonator. The spatial profile of laser beam is affected by design of the optical resonator, which includes geometry of optics, and the gain in the resonator cavity. Impurities in the lasing medium, and the pumping power affect the mode structure of the beam as well.

The beam profile is normally characterized by its transverse electromagnetic mode (TEM). The TEM is expressed by the notation TEM_{mn}, where the subscripts m and n represent the number of nodes/nulls in directions orthogonal to the beam propagation [29, 34-36]. Figure 3 shows the intensity distribution in the plane, perpendicular to the plane in which the mode distribution lies. The transverse modes can be represented in either Cartesian coordinates or in cylindrical coordinates. For rectangular symmetry in Figure 3a, the notation TEM_{mn} is interpreted as the number of nulls that occur in the spatial pattern in each of the two orthogonal directions, transverse to the direction of the beam propagation. For cylindrical symmetry in Figure 3b, the integer m indicates the number of nulls in radial direction, and n indicates half the number of nulls in an azimuthal direction. The modes marked by asterisk are linear superposition of two modes operating simultaneously 90° out of phase.



Figure 3. Laser beam profile by transverse electromagnetic mode (TEM); a) rectangular symmetry, b) cylindrical symmetry [36].

Generally, gas lasers have well defined rectangular or cylindrical symmetries in the cross section. However, spatial patterns of solid lasers, such as ruby and Nd:YAG, can not be described in simple mathematical terms, because of complicated spatial patterns [32]. This complexity in spatial patterns is caused from inevitable imperfections within the lasing media of the solid crystals.

2.1.2-b. Power Density

Depending on the average power of the laser, a typical pulsed laser produces 10^{15} to 10^{30} photons per second. In contrast a typical hollow cathode lamp produces 10^6 to 10^8 photons per second at a single wavelength [30]. The power of a laser, even with

moderate power in a few milliwatts, is orders of magnitude greater than that of the brightest conventional light source. The solid-state lasers recently have reached an average maximum of power of about 1 kW. Substantially high powers are obtainable from gas laser, which is suitable for industrial applications. Commercial continuous-wave lasers have typical power range from less than a milliwatt to tens of kilowatts. Comparable average power range is available for pulsed lasers as well. Using focusing optics, the power of a laser beam can be concentrated into a very small spot. The focused laser beam increases power density, which is usually expressed by the laser irradiance (W/cm²). The irradiance is the measure of the transferred laser power per unit cross-sectional area of the laser spot. Pulsed lasers, with the laser irradiance in excess of 10^{12} W/cm², are now available from relatively small systems [37]. Laser irradiation, with very high power density, induces an instantaneous evaporation of the solid. This laser ablation is essential for the laser spectroscopy, laser vapor deposition, and micromachining [38].

2.1.2-c. Pulse repetition

The maximum pulse repetition rates vary widely for types of lasers. Ruby and Nd:Glass lasers can generate at most a few tens of pulses per second (pps). The excimer lasers have wide range of pulse repetition rate up to a thousand pulses per second. Pulse repetition rate, duration, and peak power can also be adjusted by a variety of laser accessories such as Q-switches, mode lockers, and cavity dumpers. The temporal width of a pulsed laser is important for laser-based micromachining. Nanosecond (10^{-12} s), and femtosecond (10^{-15} s) pulses are commercially available for various applications [29, 33, 37].



Figure 4. Wavelength ranges of various types of lasers [29].

2.1.3. Types of Lasers

Lasers are generally categorized by lasing medium, and pumping methods. Such lasers span the wavelength range from infrared to ultraviolet, as shown in Figure 4. According to the general classification, lasers are grouped as dye, semiconductor, solid-state, and gas (CO₂ and excimer) lasers [29, 31, 33]. These lasers are briefly reviewed in this section.

2.1.3-a. Dye Lasers

Dye lasers are usually excited by lamps or pulsed lasers for pulsed operation, or by continuous lasers for continuous-wave radiation.



Figure 5. Schematic diagram for energy level of a typical laser dye, showing both the singlet and triplet states [29].

The lasing mechanism of liquid-state dye laser is based on fluorescent transitions in large organic molecules in solution. The energy levels associated with organic dyes, suspended in solvents, are shown Figure 5. There are two sets of energy levels in which excitation and decay can occur [29]. These are singlet and the triplet manifolds, which refer to S and T in Figure 5, respectively. The various electronic energy levels of S_0 , S_1 , T_1 and T_2 are associated with vibrational and rotational energy levels in the case of simpler molecules. When the dye laser is externally pumped, excitation occurs from the ground state S_0 to the excited state S_1 . If the excitation or pump energy occurs over broad spectra, all of the vibrational states of S_1 can be populated. However, decay of the rotational and vibrational levels in S_1 occurs very rapidly to the lowest excited level in S_1 . The accumulation of population at the lowest level of S_1 creates the population inversion between S_1 and S_0 . The stimulated emission occurs by the slow decay to S_0 , which is the

radiative transition creating laser. The triplet states essentially form separate molecules that are only weakly coupled to the singlet states by weak radiative or collisional interactions. Since T_1 lies below S_1 , some of the population in S_1 can decay to T_1 . The population will then accumulate in T_{I} , since the weak decay from T_{I} to S_{0} occurs in longer time. Thus, when excessive population moves from singlet state S_1 to the triplet state T_i , the triplet state absorption of a dye can reduce or cancel the laser gain produced in the singlets. Due to this fact, the optical resonator mechanically flows the dyes in the excitation region to physically remove the triplet state population, and to enhance laser output from the singlet system. Depending on the dye used, the output wavelength of the liquid-state dye laser can be tuned from the near-ultraviolet through the near-infrared range, typically 340 nm to 1 μ m. The use of frequency-doubling crystals can extend emission further into the near-ultraviolet. The active medium in a dye laser is a fluorescent organic dye dissolved in a liquid solvent. Over 200 dyes are available for lasing medium [39]. Dyes are large fluorescence molecules containing conjugated double bonds with multiple rings, and have complex spectra. The most widely used example is rhodamine 6G, which has wavelength output near 580 nm [39]. Major drawback of the dye lasers is photo-degradation of the dye, due to the external light or laser pumping. Rhodamine 6G has a lifetime of about 2000 watt hours, and many other long-wavelength dyes have lifetimes of several hundred watt hours. Dyes are usually dissolved in organic solvents such as methanol, and dimethylsulfoxide. Solvents of the liquid-state dye also affect both optical properties and degradation of laser dyes. In order to be useful in a dye laser, the solvent must be transparent both to the pump radiation and to the laser wavelength.



Figure 6. Schematic illustration of fundamental lasing mechanism in a semiconductor laser [29, 40].

2.1.3-b. Semiconductor lasers

Diode lasers, based on the various semiconductor materials have proved to be unique tools in various applications. The fundamental physics of the semiconductor is illustrated in Figure 6 [29, 32, 40]. Excitation of the semiconductor material, which can be provided either optically or electrically, can transfer electrons from the valence band to the conduction band. When the electrons are moved to the conduction band, the vacant sites in the valence band are referred to as positively charged holes. Electrons can decay from the conduction band to the valence band by "recombining" with the holes, since these positively charged holes are attracted to the negatively charged electrons in the conduction band. When the recombination occurs, the electrons can radiate the their excessive energy by [29]:

$$E_c - E_v = E_G = hv$$
 Equation 3

...

where E_C is energy state in the conduction band, E_V is energy state in the valance band and E_G is the band gap energy. The recombination radiation is equivalent to spontaneous emission, and following stimulated emission in other types of lasers. Semiconductor lasers have a diode configuration, which contains both the p-type (electron acceptor), and n-type (electron donor) materials. By applying an electrical potential in forward bias mode across a diode junction, electrons crossing the semiconductor boundary drop down from the conduction band to the valence band, emitting radiation by an electron-hole recombination process.

Some of the major semiconductor lasers and their wavelengths are listed in Table 1 [29]. The distinctive advantages of diode lasers are their small size, easy operation, economical configuration, high electricity-to-light conversion efficiency, and long lifetime (about 105 hours) [31].

2.1.3-c. Solid-state lasers

Solid-state lasers refer to all optically pumped lasers, which have the solid gain medium. The active lasing medium in solid-state lasers is generally a transparent crystal or glass, which is doped with less than 1% of transition metals. Most common dopants are chromium in the ruby laser, and neodymium in the Nd:YAG or Nd:Glass laser [32].

The first-invented ruby laser has the three-level pumping scheme as shown in Figure 7 [29]. A flash-lamp is the pumping source for the ruby laser.

Compound	Wavelengths (nm)	Notes
ZnSe	525	First demonstrated in 1991
AlGaInP	630-680	Developmental; lifetimes have been short at
		shorter wavelengths
Ga _{0.5} In _{0.5} P	670	Active layer between AlGaInP layers; long room
		temperature lifetime
Ga _{1-x} Al _x As	620-895	x = 0 to 0.45; lifetimes very short for
		wavelengths below 720 nm
GaAs	904	
In _{0.2} Ga _{0.8} As	980	Strained layer on GaAs substrate
In _{1-x} Ga _x As _y P _{1-y}	1110-1650	InP substrate
In _{0.73} Ga _{0.27} As _{0.58} P _{0.42}	1310	Major fiber-communication wavelength
In58Ga42As09P0.1	1550	Major fiber-communication wavelength
InGaAsSb	1700-4400	Possible range; developmental; on GaSb
		substrate
PbEuSeTe	3300-5800	Cryogenic
PbSSe	4200-8000	Cryogenic
PbSnTe	6300-29,000	Cryogenic
PbSnSe	8000-29,000	Cryogenic

Table 1. Major semiconductor lasers and their wavelengths [29].

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Figure 7. Schematic diagram for energy level of the three-level ruby laser [29].
Pumping is achieved by absorption of the pump light on transitions from the ground level to the ${}^{4}F_{1}$ excited level in the blue spectral region, and to the ${}^{4}F_{2}$ excited level in the green. Since both of these transitions have a broad absorption spectrum, a broad-spectrum pumping lamp can be used with reasonable efficiency. The population pumped to these excited states nonradiatively decays to the ${}^{2}E$ state, where a population inversion builds up with respect to the ground state ${}^{4}A_{2}$. Lasing by stimulated emission occurs between the intermediate state ${}^{2}E$ and the ground state ${}^{4}A_{2}$. The stimulated emission has a wavelength of 693.4 nm. The optical resonator of ruby is often equipped with a Q-switch, which controls the output by concentrating all of the energy into a single, intense pulse with duration of about 25 ns. A single pulse can have powerful 10 J or more of energy. The pulse repletion is restricted by heating of ruby rod, hence, the optical resonator generally has cooling system. The typical emission bandwidth of the ruby laser is about 0.5 nm. The beam diameter of a low-power ruby laser can be as little as 1 mm, with the beam divergence of about 0.25 milliradian [33].

Neodymium lasers have two major types: neodymium-doped yttrium aluminum garnet (Nd:YAG), and neodymium-doped glass (Nd:Glass) lasers. Even though the emission characteristics are slightly different due to the influence of the host lattice on the neodymium energy level, transitions in the neodymium ions are responsible for laser action in both the Nd:YAG and Nd:Glass lasers [29]. The energy-level diagram for Nd:YAG is shown in Figure 8. Excitation occurs by optical pumping from the ${}^{4}I_{9/2}$ ground state to a band of excited states. Rapid and nonradiative decay occurs to ${}^{4}F_{3/2}$ upper laser level, where a population inversion builds up with respect to the ${}^{4}I_{11/2}$ lower laser level.



Figure 8. Schematic diagram for energy level of the four-level Nd:YAG laser [29].

The stimulated emission of a wavelength of 1.06 μ m occurs between the upper and lower laser levels. After the stimulated emission, another nonradiative decay follows very rapidly between the ${}^{4}I_{11/2}$ lower laser level to the ${}^{4}I_{9/2}$ ground state. For Nd:YAG laser, the output energy at 1.064 μ m ranges from a tenth of watt to hundreds of watts. Particularly useful shorter-wavelengths of 532, 355, and 266 nm can also be obtained by harmonic generation [33]. By Q-switching or mode locking, pulsed output can be obtained from continuously pumped Nd:YAG lasers. The divergence of Nd:YAG laser beams can be from a fraction of around 1 to 10 milliradian, and beam diameter is 1-10 mm. The Nd:Glass laser produces laser radiation at 1.05 μ m. The glass lasing medium in the Nd:Glass laser has several advantages over the YAG. Since the glass is isotropic material with cheap and easy fabrication, it can be doped with a large concentration of neodymium to produce higher power than YAG. However, the glass has a lower thermal conductivity, which prohibits continuous-wave operation. The low thermal conductivity also limits the pulse repetition rate in pulsed operation [29, 31, 33].

<u>2.1.3-d. CO₂ lasers</u>

The carbon dioxide laser is one of the most powerful lasers. The energy levels involved in carbon dioxide laser action are rotational and vibrational levels, and emission therefore occurs at much longer wavelengths in the infrared region [34].

The CO₂ molecule is a linear triatomic molecule with three normal modes of vibration, which are the symmetric stretch mode, the bending mode, and the asymmetric stretch mode, as shown in Figure 9a. Thus, the CO₂ molecule has three separate quantum numbers v_1 , v_2 , and v_3 , which have values of non-negative integers. The total energy associated with a given energy level of this molecule would be described by an expression with three quantum numbers [34]:

$$E_{total} = (v_1, v_2, v_3) = h v_1 \left(v_1 + \frac{1}{2} \right) + h v_2 \left(v_2 + \frac{1}{2} \right) + h v_3 \left(v_3 + \frac{1}{2} \right)$$
 Equation 4

This equation represents the energy state above the ground state of the molecule. At the ground state in Figure 9b, the molecular energy is equal to $E(0,0,0) = \frac{1}{2}(hv_1 + hv_2 + hv_3)$, which is the lowest energy of the molecule. As shown in Figure 9b, the most well-known transition of the CO₂ laser involves the radiative transition from E(0,0,1) to E(1,0,0), which generates infrared laser at 10.6 µm. The transition from E(0,0,1) to E(0,2,0) also generate radiative emission at 9.4 µm [34].



Figure 9. Lasing mechanism of CO_2 laser, a) vibrational modes of CO_2 molecule, and b) laser transitions among vibrational levels of CO_2 laser [29].

The carbon dioxide gas is usually accompanied by nitrogen and helium. Most carbon dioxide lasers are discharge-pumped, and occasionally RF excitation is used. The discharge is pulsed at a rate of about 20 per second, and produces output of hundreds of kilowatts. In CO_2 lasers, nitrogen and helium are used for collision partner, which transfer energy to CO_2 molecules by collisions. Oscillation occurs between two vibrational levels in carbon dioxide, while the nitrogen and helium greatly improve the efficiency of laser action. The output power of the laser can be increased by use of the Q-switch technique [31, 36].

Generally, carbon dioxide lasers are categorized into six types by their nature of constructions, such as longitudinal flow lasers, sealed-off lasers, waveguide lasers, transverse flow lasers, transversely excited atmospheric pressure (TEA) lasers, and gas-dynamic lasers [31]. Maximum output depends on the type of carbon dioxide laser. Waveguide lasers can produce continuous-wave output up to about 50 W, while sealed carbon dioxide lasers can reach about twice that level. Longitudinal flow lasers can reach the kilowatt range, while transverse-flow lasers can produce several kilowatts. Average powers of TEA lasers range up to a few thousands watts. The powerful 10.6 μ m emission of carbon dioxide is ideal for variety of materials processing, such as drilling, cutting, cladding, and welding.

2.1.3-e. Excimer lasers

Excimer is usually defined as a molecule that is bound only in the excited state. The word "excimer" is originated from "excited dimer," meaning an excited diatomic molecule.

type	excimer	wavelength (nm)	
	Ar ₂	126	
rare gas dimers	Kr ₂	146	
F	Xe ₂	172	
halogen dimers	F ₂	157	
	KrO	558	
rare gas oxides	XeO	537.6 and 544.2	
	ArF	193	
F	KrF	248	
rare gas halides	XeF	351 and 353	
F	KrCl	222	
	XeCl	308	
	HgCl	558	
metal halides	HgBr	503 and 498	
	HgI	444	

Table 2. Various types of common excimers and their wavelengths [33].

The excimer molecules exist only in excited states, because two constituent atoms are repulsive to each other in the ground state [29]. Excimer molecules disassemble immediately upon falling into the ground state. Excimer lasers are a group of pulsed lasers that incorporate electronic transitions of the excited molecules. Such lasers are most often composed by the combination of a rare-gas atom (such as Ar, Kr, or Xe) and a halogen atom (Fl, Cl, Br, or I). Table 2 shows common excimers and laser wavelength generated from them. Most excimer lasers typically emit in the ultraviolet spectral region, and some others emit the visible spectrum.

The lasing mechanism for excimer laser can, in a simplified sense, be viewed as a sequence of collisional energy exchanges [33]. As shown in Figure 10, the lasing mechanism for excimer laser is explained in the following with an example of KrF, which is one of the most powerful and the most commonly used excimer lasers.



Figure 10. Lasing mechanism of KrF excimer laser.

Since the outer shell of rare-gas (Kr) atom is already saturated, a bound state is not formed between the rare-gas (Kr) and halogen (F). In ionization process, excited state of Kr and F atoms are formed by electrical discharge [33]:

$$Kr + e^- \rightarrow Kr^+ + 2e^-$$

 $F_2 + e^- \rightarrow F^- + F$ Equation 5

The positively charged Kr^* ion can enter molecular bond with a negatively charged F ion by Coulomb interaction. However, reaction of the excited state of the excimer, KrF^* , requires extra kinetic energy. A collision partner helium acts as a buffer gas, and transfers extra energy by collision [33]:

$$Kr^+ + F^- + He \rightarrow KrF^+ + He$$
 Equation 6

where '*' signifies the excited state. The formation of the KrF^{*} excimer is the result of a threefold collision among krypton, fluorine, and helium.



Figure 11. Construction of a typical excimer laser showing optical resonator of electron beam discharged KrF excimer laser.

After rapid decay to intermediate energy state, the transition of excimer to the ground state induces the stimulated emission, which generates radiative emission at 248 nm by [33]:

$$KrF^* \rightarrow Kr + F + hv$$
 Equation 7

An excimer laser can be technically realized with the excitation using either an electron beam or by means of a gas discharge. Figure 11 shows construction of a typical excimer laser, which illustrates structure of the optical resonator of electron beam discharged KrF excimer laser [29, 33]. Due to the corrosive nature of the halogen species, the entire structure is made of stainless steel with poly vinyl and Teflon components. The cathode emits electron-beam radiation to produce ionization of lasing medium. The discharge current is provided by discharging a high-voltage capacitor, using a thyratron switching device. Generally, the output is obtained by using a totally reflecting mirror at the rear of the laser, and partially reflecting quartz mirror at the output front.

The most common excimer lasers are XeF at 351 nm, XeCl at 308 nm, KrF at 248 nm, and ArF at 193 nm [37]. The typical pulse energy ranges from 0.5 J to 2 J, and average pulse duration ranges from 5 ns to 50 ns. Output power is determined by pulse repetition rate, which generally ranges from a few pulses per second to 200 pulses per second. Excimer lasers are used primarily for materials processing, medical applications, photolithography, and pumping of dye lasers. In the materials processing area, excimer lasers are advantageous because of their wavelength and energy per pulse. Generally, materials processing requires the laser irradiance over 10^6 W/cm², which can be easily obtained by an excimer laser [38]. Also, the absorption coefficient for most materials is much greater for ultraviolet wavelengths than for visible and near-infrared wavelengths. Hence, excimer laser beams are absorbed over a much shorter depth, when materials are irradiated with such lasers. This enables the production of sharper edges in ablation processes. This is also advantageous for such medical applications as laser surgery and corneal sculpting, which provides optical correction without the need for eyeglasses. In the lithography field, the excimer laser provides a good ultraviolet illumination source at 248 nm and eventually at 193 nm for producing microchip features [37, 38]. Excimer lasers are also used for the pumping of dye lasers, since all dyes have an extended absorption into the ultraviolet.

2.2. CVD diamond film

Carbon exists in three general types of inorganic solid structures, such as graphite, diamond and Buckyball, as shown in Figure 12 [2-4, 41]. In graphite, carbon atoms are structured by three coplanar bonds (sp^2 type) in bonding length of 1.42 Å. The coplanar bonds form regular hexagons in monoplanes, which are connected by interplanar bonds in bonding length of 3.35 to 3.44 Å. These long interplanar bonds are very weak bonds, which are broken by even a small force, resulting in the lubricating properties of graphite. Most forms of inorganic carbons consist of disordered fragments of the graphite structure. In diamond, carbon atoms form tetrahedral bonds (sp^3 type) in bonding length of 1.54 Å. The (sp^3 type) bonding results in an extremely rigid, tight and strong structure. The third structure of carbon after graphite and diamond is the Buckyball, which is named for the reminiscence of the discoverer, R. Buckminster Fuller. The Buckyball is made up of 28 to 540 carbon atoms in hexagonal and pentagonal arrays. The most stable structure is the well known C⁶⁰, which is composed of twelve pentagonal and twenty hexagonal arrays.

2.2.1. Growth of CVD diamond

Chemical vapor deposition (CVD) involves a gas-phase chemical reaction occurring in a controlled environment, which causes deposition of the reactants onto a solid substrate [2]. The reactants for the synthesis of CVD diamond are typically a small amount of methane (CH₄) in hydrogen (H₂) at pressures between 10^2 Pa (~ 1 torr) and 10^5 Pa (~ 1 atm).





(c) C⁶⁰ Buckyball

Figure 12. Three general types of inorganic carbon structures; a) graphite, b) diamond, and c) Buckyball.

Variations of the CVD processes for diamond include carbon monoxide, oxygen, hydrocarbons and nitrogen. The CVD process for the diamond is schematically shown in Figure 13[2]. The gaseous reactants, typically less than 5% of methane in hydrogen matrix, flow into the reactor. The CVD process for producing diamond films requires the activation of the gaseous reactants. The general methods for the activation are to use a combustion flame, a hot filament, and a plasma induced by DC, RF, or microwave.



Figure 13. Schematic diagram for the chemical vapor deposition of diamond [2].

The gaseous reaction is initiated by dissociation of the molecular hydrogen into atomic hydrogen. The activation can be achieved by thermal dissociation on a hot filament or by electron impact dissociation in plasma [42-44]. The subsequent chemistry is driven by a series of reactions, in which the activated atomic hydrogen reacts with hydrocarbon species. These activation and subsequent chemistry is generally remote from the deposition surface. Transport of carbon atoms to the deposition substrate is carried out by diffusion and convection [1, 2].

Figure 14 shows the schematic illustration for the carbon phase diagram [3].



Figure 14. Schematic illustration for the carbon phase diagram, and fabrication regions for synthetic diamonds. The CVD diamond exists metastably in the graphite region [3].

The stable phase in the diagram is graphite at lower pressures, diamond at high pressure, and liquid at extremely high temperatures. The various methods for the fabrication of synthetic diamonds are indicated in the carbon phase diagram. The process by dynamic explosive shock wave is shown in the top area of the diamond region, and the processes by the high-temperature and high-pressure is shown in the lower area of the diamond region. At the bottom of the diagram in the graphite region, the diamond is synthesized metastably by CVD at pressure less than the ambient atmosphere and at temperature near 1000 °C. Since the CVD diamond exists in metastable state, it is converted to graphite when it is heated to about 1000 °C or greater [3]. In the CVD process, the resulting films are polycrystalline, with a morphology that is sensitive to the precise growth conditions. Texture and morphology of CVD diamond films primarily depends on methane concentration and substrate temperature. These processing conditions determine the growth parameter, $\alpha = (V_{100}/V_{111})\sqrt{3}$, where V_{100} and V_{111} describe the ratio of the growth rates on {100} and {111} planes, respectively [45]. In epitaxially textured diamond films, which are grown on {100} single crystal silicon wafer, the growth parameter results in various distinctive textures and surface morphologies.

Growth of CVD diamonds is a chemical process, which takes place by incorporation of carbon atoms into the crystal lattice [2]. The carbon atoms in the diamond lattice are linked by strong sp^3 covalent bonds. Crystal planes of diamond films, such as {100}, {110} and {111} exhibit different planar densities and surface energies. Dangling bonds on the surface of CVD diamonds are terminated by hydrogen atoms. According to these crystallographic properties, Figure 15 shows geometry of hydrogen terminated (100), (110), and (111) plane of a diamond lattice. For the (100) plane in Figure 15c, ideal hydrogen truncation, which locates the adjacent hydrogen atoms closer than molecular hydrogen, give rise to violation of steric constants. An example of generalized reconstruction is shown in Figure 15d, which compensates steric constants and lattice distortion [2, 46].

Growth rates for the CVD processes vary considerably, and generally, the higher growth rates can be achieved by the expense of a corresponding loss of film quality [1].



Figure 15. Geometry of hydrogen terminated (100), (110), and (111) plane of a diamond lattice, a) (111) plane, b) (110) plane, c) (100) plane, d) reconstructed (100) plane. Large and dark circles represents carbon atoms, and small and light circles represents hydrogen atoms [2].

The quality of the CVD diamond films is related to some factors, such as the ratio of sp^3 to sp^2 bonding, hydrogen (C-H bond) contents, and the crystallinity [43, 47-50]. In general, CVD processes with combustion activation deposit diamond at high rates, typically 100 to 1000 μ m/hr. However, the process is limited to a localized area, and the quality of the deposited diamond is poor due to the poor controllability of the combustion process. In contrast, the hot filament and plasma methods produce high quality diamond films, however these activation methods have much slower growth rates, typically 0.1 to 10 μ m/hr [51].

	CVD diamond	other materials	ratio (diamond to other materials)
elastic modulus	1035	393 (Al₂O₃)	2.6
(Gpa)		186 (Ti)	5.5
Knoop hardness	7000	2190 (WC)	3.2
(kg/mm ²)		800 (Hardened steel)	8.7
thermal conductivity	20	3.80 (copper)	5.3
(Watts/cm-°C)		1.5 (graphite)	13.3
friction coefficient	0.05	0.10 (lubricated metals)	0.5
(friction force/normal thrust)		0.10 (graphite)	0.5
bandgap	5.45	1.10 (silicon)	5.0
(eV)		1.43 (GaAs)	3.8
resistivity	10 ¹⁶	10 ³ (silicon)	10 ¹³
(Ω-cm)		10 ⁹ (GaAs)	10 ⁷

Table 3. Comparison of material properties between CVD diamond and other materials [3-5, 41].

2.2.2. Properties of CVD diamond

CVD diamond film inherits superior material properties of a natural diamond. The strong sp^3 covalent bonding among carbon atoms gives rise to unmatched material properties of diamond. Various material properties are compared between diamond and other materials in Table 3. The ratios in the last column of Table 3 indicate the diamond to other materials ratio in the given material property. One of the great properties of diamond is its chemical inertness. CVD diamond resists almost all forms of chemical attack at room temperatures. CVD diamond can be safely cleaned in strong reagents such as boiling sulfuric acid and hydrofluoric acid. However, due to the metastable existence of diamond, it has been oxidized at high temperatures in caustic alkalis and monatomic gases such as oxygen and hydrogen [52].

The extremely high elastic constants of diamond make the values of moduli, strength, and hardness the highest of any other materials. Like other ceramic materials, pure diamond is brittle and exhibits low fracture toughness. On the contrary, the fracture toughness for polycrystalline diamond is considerably higher. This is mainly due to the presence of a second phase from the CVD process. In addition to its high strength and hardness, diamond also exhibits the lowest friction coefficient of any solid material, as well as the ability to propagate sound at high velocities [3, 4, 41, 52, 53].

Diamond possesses many unmatched electron properties as well. It has the highest electrical resistivity of materials. Theoretically, ideal diamond should exhibit resistivity near $10^{70} \Omega$ ·cm. However, impurities reduce this value considerably so that resistivity value near $10^{16} \Omega$ ·cm is observed for CVD diamond. As a semiconductor, diamond exhibits the highest saturated electron velocity, the lowest dielectric constant, the highest dielectric strength, and the largest band gap of any semiconducting material. The common acceptor (*p*-type) impurity in CVD diamond is boron [52].

One of many remarkable properties of diamond is its thermal conductivity. In contrast to metals, where conduction electrons are responsible for the high thermal conductivity, heat is conducted in electrical insulators by lattice vibrations. This thermal conductivity of diamond comes from phonon heat transfer, which proceeds readily across diamond's tetrahedral crystal lattice of low-atomic-mass atoms and stiff covalent bonds [41]. The thermal conductivity of diamond is about five times larger than that of copper. Diamond also exhibits the lowest specific heat and highest Debye temperature of all solid substances.

Diamond has the widest spectral transmission range (225 nm to 25 μ m) of all known solids. It exhibits high transparency throughout the visible, near infrared, and thermal infrared wavelengths. Theoretically, ideal diamond is absolutely transparent to visible light, but impurities and defects in CVD diamond cause absorption in visible

region. Diamond also shows luminescence, which can be excited by electricity, phonon irradiation or particle bombardments. The luminescence takes the form of fluorescence, phosphorescence, or thermo-luminescence [3-5, 41].

2.2.3 Applications for CVD diamond

The superior material properties of CVD diamond have exhibited a great potential in various applications. Recent successful developments of vapor-phase-growth technology have made large-area deposition available at low production cost, and these have expedited the industrial applications of CVD diamond. The commercialization of diamond is limited at current state, leaving great opportunities for future applications. Currently, the major applications for CVD diamond are in the limited areas of coated tools, speaker diaphragms, and heatsinks. However, substantial progresses in research have been accomplished for near-future applications in sensors, optical windows, semiconductor devices, field emitters and MEMS [53].

2.2.3-a. Coated tools

CVD diamond has been applied as a coating on cutting tool inserts. CVD diamond-coated drill bits, reamers, and countersinks are now commercially available for machining non-ferrous metals, plastics, and composite materials. The CVD diamond-coated tools have exhibited a longer life, a shorter machining time, and a better finish, as compared to conventional tungsten carbide tool bits. However, the application for coated tools is limited to the non-ferrous machining. In any application of coated tools, the diamond will be heated up due to the involved friction. Carbon has strong interstitial affinity to ferrous materials. In case of machining of iron or steel, the diamond coating

reacts with the workpiece, and dissolves into it. Research efforts are currently underway to place suitable barrier-layer materials to allow machining on iron and steel with diamond-coated inserts. Diamond coatings for large-area wear resistance are also currently in progress. These coatings will greatly increase, with reduced lubrication, lifetimes of large components, such as gearboxes, engines, and transmissions [3, 4, 41, 52, 53].

2.2.3-b. Heatsink

Diamond, as an electrical insulator, has a thermal conductivity about five times superior to that of pure copper. Diamond has been investigated for heatsinks, and applied to heat sinks for laser diodes, and for small microwave integrated circuits. For integrated circuits, devices mounted on diamond can be packed more tightly without overheating. Reliability can also be expected to improve from lower junction temperatures. Diamond also retains excellent insulating and dielectric characteristics. These superior properties make CVD diamond an excellent candidate as a packaging material for high power and high frequency components. However, diamond has a smaller coefficient of thermal expansion (CTE) than that of other semiconductor materials. Mismatching of CTE, between diamond and semiconductor device, can cause cracks at the interface. Thus, the die size on a diamond heatsink is limited to several hundred microns. For larger heatsink, various research efforts are currently undergoing to reduce the drawbacks from the CTE mismatch [3, 4, 41, 52, 53].

2.2.3-c. Optical windows

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Diamond has the highest transparency in wide range from infrared to x-ray. Due to these excellent optical properties, diamond can be coated to optical components. Diamond has been successfully adopted as a protective coatings for infrared (IR) optics in harsh environments. Most IR windows are currently made from materials such as ZnS, ZnSe, and Ge. These materials have excellent IR transmission characteristics, but are brittle and easily damaged. A thin protective barrier of CVD diamond coating provides the answer for the IR optics. The IR windows can also be made from freestanding diamond films, which can be grown to a thickness of a few millimeters. Since rough surface of polycrystalline CVD diamond can cause attenuation and scattering of the transmitted IR signal, technical developments for polishing diamond surface have to be accompanied with the application to the optical windows [3, 4, 41, 52, 53].

2.2.3-d. Semiconductor devices

Diamond retains semiconducting properties with a large energy band gap of 5.45 eV and a relatively small lattice constant, compared to other semiconductors. Even though these properties make diamond films difficult to form a semiconductor with hetero-junctions, the large band gap is a unique characteristic of diamond for high temperature and high power operation, associated with its high thermal conductivity. The doping of diamond changes it from an insulator to a semiconductor, and opens up new range of potential electronic applications. However, major problems have to be solved to achieve practical application of diamond-based electronic circuits.

One of the major problems is the difficulty to produce n-type doped diamond film. The p-type doping is currently possible by incorporation of boron atoms into the diamond lattice. This incorporation of boron atoms is achieved by addition of a few percent of B_2H_6 to the gas mixture for CVD process. However, the doping, with atoms larger than carbon, is very difficult due to the close packing and rigidity of the diamond lattice. The *n*-type doping typically involves dopants like phosphorus or arsenic atoms, which are larger than carbon atoms. Alternative dopants such as lithium are currently investigated for the n-type doping on CVD diamond. Another problem is that CVD diamond is grown with polycrystalline assemblies, which contain grain boundaries, twins, stacking faults, and other defects. All of these reduce the lifetime and mobility of carriers [53].

One further difficulty is to achieve patterning on diamond film. The patterning is essential to engrave circuits in required micron or even submicron geometries. Dry etching, using oxygen-based plasmas, can be used, but it involves very slow etching rates with complex procedures. Alternative patterning method is the selective nucleation by lithography-patterned diamond growth. In the process, a lithography-patterned photoresist layer, in which diamond seeds are embedded, is placed in CVD reactor for the diamond growth. Besides its step-intensive procedure, the process exhibits lateral growth of diamond film, which limits the resolution and aspect ratio of the patterned structure [54-57].

Despite these difficulties, remarkable research efforts have been exerted on CVD diamond-based semiconductor devices. Piezoelectric effect devices, radiation detectors, and the first field-effect transistors have been reported recently from laboratories, as a prelude to the commercial diamond devices. Especially, application of diamond, as an electron emitter in flat panel displays, draws a great deal of attention at the current moment [52, 53].

2.2.3-e. Sensors and MEMS

Various sensor applications for CVD diamond are currently under investigations, including a pressure sensor using piezoresistivity, a thermistor using electrical conductivity, a photodetector using photoconductivity, and a cantilever sensor for atomic force microscopy. Currently, most of the MEMS devices have been based on silicon. This is due to the technology, which has been accumulated in manufacturing of siliconbased semiconductor. Since these silicon-based systems have exhibited rapid wear from high friction of the system, only very few MEMS devices involve actual mechanical operation. The excellent material properties in friction, wear, and thermal conductivity make CVD diamond uniquely qualified for MEMS applications. To utilize the excellent properties of the diamond films in sensor and MEMS applications, micromachining and patterning of diamond films are primarily required. For CVD diamond, conventional machining and lithography-based patterning are difficult due to the high wear resistance and the chemical inertness. Recently, such as in this research, the pulsed laser ablation has been demonstrated as a new method for making patterned structures and microcomponents on CVD diamond [52, 53].

Chapter III

EXPERIMENTAL

3.1. CVD Diamond Films

Diamond syntheses by CVD, as reviewed in Chapter 2, have been developed by various thermal activation methods of gaseous reactants [3-6, 43, 45, 58]. The reactant gas mixture includes mainly a small amount of CH_4 (< 5%) in H₂ gas matrix, with some other supplementary gaseous species. The activation of the reactants is achieved by various energy sources, such as hot filaments, plasmas, and combustion flames [6]. Among the vapor phase processes, microwave plasma assisted CVD method has been extensively practiced by virtue of its distinctive advantages. These advantages include reduced contamination, higher concentration of activated reactants, and centralized deposition process [43]. To grow high quality, and large area diamond films, a 7-inch microwave cavity plasma reactor (MCPR7) has been developed in the Micro and Nano Engineering Center at Michigan State University [43]. All polycrystalline diamond films in our research study have been processed in the third generation MCPR7. Figure 16 shows the schematic diagram for the MCPR7. The mass flow controllers regulate and mix the reactant gases (H₂, CH₄ and CO) before they are introduced in the reaction chamber. The microwave power supply (Carber, model S6F/4053) is the variable microwave power source with maximum output of 6 kW at 2.45 GHz.



Figure 16. Schematic diagram for the 7-inch microwave cavity plasma reactor (MCPR7) at Michigan State University [43].

The mechanical roughing pump is used to pump down the chamber pressure up to -0.01 torr. The flow of nitrogen gas near the exhaust dilutes the exhaust gas mixture, which is hot and flammable. The entire vapor deposition process can be monitored and controlled by a computer controller. All diamond films used in our research study were hetero-epitaxially grown on 2-inch or 3-inch diameter single crystal silicon wafer, as shown in Figure 17.



Figure 17. Hetero-epitaxially grown diamond films on 2-inch-diameter and 3-inchdiameter single crystal silicon wafers.

Texture and morphology of CVD diamond films primarily depend on methane concentration, and substrate temperature. In hetero-epitaxially textured diamond films, which are grown on {100} single crystal silicon wafer, the growth parameter results in various distinctive textures and surface morphologies. In this investigation, diamond films with {100}, {111} and mixed surface morphologies are chosen to be subjected to the excimer laser ablation. The grain size and vertical thickness of the subjected diamond films ranged from 2 μ m to 50 μ m, and form 4 μ m to 270 μ m, respectively. The processing parameters for the all CVD diamond films used in this study is listed Table 4, where *P* is the chamber pressure, *T_r* is the silicon substrate temperature, *CH_s/H₂* is the methane concentration, *time* is the reaction time, *G_x* is the average grain size, *V_t* is the average vertical thickness and *ref*, is the reference for the processing parameters.

notation	P (torr)	T_s (°C)	$CH_{1}/H_{2}(\%)$	time (h)	$G_{s}(\mu m)$	V_t (µm)	ref.
AT109	80	845	2	8	2	7	[44]
BW062	38	850	2	8	2	4	[59]
BW097	38	860	1	8	2	6	[59]
ST204	120	1060	3	75	40	270	[44]
ST235	135	1057	3	20	50	110	[44]

Table 4. Processing parameters for the CVD diamond films used in this study.



Figure 18. Cross section of free standing diamond film (ST204) showing the rough film surface of diamond-growth side (upper surface), and the flat surface of the substrate side (lower surface).

Among the diamond films in Table 4, ST204 and ST235 are the freestanding diamond films. To acquire a freestanding diamond film, the silicon wafer substrate, where the CVD diamond film was grown by the hetero-epitaxial growth, was completely dissolved in the etching solution (50%HNO₃ + 25%HF + 25%CH₃COOH). The substrate side of the freestanding diamond film retains flatness similar to that of the polished silicon wafer. The cross section of the freestanding diamond films (ST204) is shown in Figure 18.

3.2. MP-I Maskless Patterning System

The innovative maskless patterning technique employs pulsed irradiation of a focused laser beam on a target material, which is translated to the programmed positions by a micro computer numerical controlled (micro-CNC) stage. To produce micro patterns, and structures using laser ablation technique, the maskless patterning system MP-I has been constructed in the High Energy Laser Processing Laboratory (HELP) at Michigan State University. Figure 19 shows the overview and the schematic of the MP-I system, which is mainly composed of an excimer laser, imaging optics and the micro-CNC stage. The components of the MP-I system are discussed in next sections.

3.2.1. Excimer laser

A KrF excimer laser, COMPex 301 manufactured by the Lambda Physik[®], was used for the MP-I maskless patterning system. The excimer laser has the wavelength of 248 nm from the lasing medium of krypton fluoride. It has a rectangular pulsed beam in TEM₀₀ mode. The maximum pulse energy from its resonator is 1.5 Joules, and the maximum repetition rate is 10 times per second (10 Hz). The premixed gas, which is composed of 2.7% krypton, 0.1% fluorine, 16.2% helium, and 81% neon, were used for the lasing gas for the excimer laser. The specifications of the laser are listed in Table 5.

The excimer laser beam from its resonator has an energy distribution profile. The rectangular beam $(13\times30 \text{ mm}^2)$ has the Gaussian profile in its vertical section and flat-top profile in its horizontal section [60]. The profile of the beam is shown in Figure 20. In the MP-I system, the apertures were placed to select the central region of the raw excimer laser beam. The uneven ablation from the beam profile was minimized by using the central region of the beam.







Figure 19. a) Overview of the MP-I maskless patterning system, designed for this research, and b) the schematic diagram of the MP-I system.

lasing medium	KrF
wavelength	248 nm
maximum pulse energy	1,500 mJ
average maximum power	15 Watt
pulse duration	25 ns
maximum repetition rate	10 Hz
beam divergence	3×1 mrad (W×H)
beam dimension	13×30 mm ² (W×H)

Table 5. Specifications of the KrF excimer laser, Lambda Physik® COMPex 301.



Figure 20. Beam energy profile of rectangular beam (13×30 mm²) from the KrF excimer laser showing a Gaussian profile in its vertical section and flat-top profile in its horizontal section [60].



Figure 21. Construction of the laser imaging system according to the thin lens principle.

3.2.2. Imaging optics

To engrave small features on a target, the construction of the laser imaging system is required according to the thin lens principle. Figure 21 shows the schematic of the laser imaging system, in which the laser illuminates the demagnified image from the mask. The thin lens principle is written as [61]:

$$\frac{1}{i} + \frac{1}{o} = \frac{1}{f}$$
 Equation 8

where i is the distance between the lens and the focused imagine, o is the distance between the mask and the lens, and f is the focal length.

The imaging optics in the MP-I system was constructed for this research according to the principles of the laser imaging system. The uniqueness of the MP-I system is that it uses small circular apertures instead of the patterned masks. The concept of the maskless patterning is the illumination of the focused small laser beam on a translating target. Various patterns can be rapidly obtained by programmed translation of the target material. The maskless patterning addresses the time consuming fabrication of the masks in the lithography-based patterning, in which each patterning requires the fabrication of a patterned mask.

The imaging optics in the MP-I system includes an automatic aperture unit, a set of planar convex lenses and the gas delivery unit. The components of the imaging optics are illustrated in Figure 22. Figure 22a shows the schematic diagram of the imaging optics. The automatic aperture unit and the beam shutter in Figure 22c are controlled by the motion stage controller (see Figure 19), and the operation can be programmed together with micro-CNC stage. The automatic aperture unit has four apertures of different sizes in a rotating disk. The DC motor, which is controlled by the motion stage controller, rotates the disk to automatically change the size of the aperture. A rectangular pulsed laser beam passes through the circular aperture, and then the circular beam is focused by the two planar convex lenses, as shown in the laser beam path in Figure 22b. Various spot sizes can be available by changing the size of apertures in the automatic aperture unit. The size of the apertures in the automatic aperture unit, and resultant focused spot sizes, at the target, are list in Table 6. The beam shutter is essential for the continuous patterning process of discrete patterns. Since the KrF excimer laser cannot be turned on and off very quickly (the excimer laser requires ~ 5 minutes of stabilization after turned on), the blocking of the laser source is required for the pattering of successive discrete patterns (for example engraving disconnected capital letters such as MSU). The beam shutter uses stepper motor, whose motion is programmed together with the micro-CNC stage. An example of the laser ablation for the discrete pattern is in shown Section 6.1.3.

Figure 22d shows the gas delivery unit, which incorporates the gas nozzles and objective lens. Three gas nozzles are installed around the objective lens, to deliver dynamic gas streaming over the irradiation spot. The nozzles are positioned about 3 mm from the irradiation spot and 30° degrees to the film surface.

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(d) dynamic gas delivery unit

Figure 22. Illustration for the components in the imaging optics in the MP-I system; a) schematic diagram for the imaging optics, b) beam path diagram for the imaging optics, c) automatic aperture unit and beam shutter, and d) gas delivery unit for the dynamic gas streaming. (these units were all designed and built for this research.)

aperture size (mm)	spot size (µm) at the target		
9.5	750		
6.3	500		
2.2	175		
1	80		

Table 6. Size of the apertures in the automatic aperture unit and resultant beam spot size

at the target.



Figure 23. Schematic diagram showing offset of the direction of the dynamic gasstreaming nozzle.

The diameter of the gas nozzles is 2 mm and the maximum gas flow rate of the unit is 12×10^4 m³/sec. The nozzles are pointing the irradiation spot, with ~ 3° offset to the center, streaming around the center of the spot. The schematic diagram in Figure 23 shows the offset of the gas nozzles for the dynamic gas streaming. The offset was set to prevent the static pressure, and to create the dynamic vortex streaming around the center of the irradiation spot.

3.2.3. Micro computer numerical control (micro-CNC) stage

In the maskless patterning system, programmed translations of target materials are required to produce micro patterns, and structures, using laser ablation technique. The micro-CNC stage has been constructed in the MP-I maskless patterning system for the programmed target translations. Figure 24 shows the schematic diagram for the motion stage in the MP-I system and the specific features of the motion stage. The micro-CNC stage contains a 5-motion-axes stage (x-y-z, rotation and tilt), which allows a target translation in three-dimensional directions. As shown in Figure 24a, the micro-CNC stage is controlled by the IBM-PC based motion stage controller, which incorporates the index module, the translator, the stepper motor driver and the DC power source. The index module is from the Microkinetics Co. (Kennesaw, GA), model OuickPhase, which can control up to 3 axes simultaneously. The index module is programmed by the software (Microsoft, QuickBasic) for the patterned translations. The motion axes synchronizer is a switcher, which can choose the 3 axes for the simultaneous motion control from the 5-motion-axes in the micro-CNC stage. The central computer in the system synchronizes the excimer laser and the micro-CNC stage, and also monitors the process through the *in-situ* observation camera.

The features of the micro-CNC stage are shown in Figure 24b, in which the X-Y-Z, rotation and tilt stages are indicated. In the micro-CNC stage, the X and Y motion stages are made by ArdelKinematic Co., and all other components are designed and constructed by the High Energy Laser Processing Laboratory.



(a) schematic diagram for the 5-motion-axes micro-CNC stage in the MP-1 system



(b) front view of the 5-motion-axes micro-CNC stage



(c) side view of the 5-motion-axes micro-CNC stage

Figure 24. 5-motion-axes micro-CNC stage in the MP-1 system; a) schematic diagram, b) front view, and c) side view. (The systems, and subsystem shown in these figures, were designed and built for this research.)

	stepper motor resolution	motion stage resolution	maximum speed	minimum speed	translation limit
X stage	7.5 °/step	4 µm/step	7.2 mm/sec	200 µm/sec	13 mm
Y stage	7.5 °/step	4 µm/step	7.2 mm/sec	200 µm/sec	13 mm
Z stage	0.9 °/step	0.025 µm/step	45 μm/sec	1.25 µm/sec	5 mm
rotation stage	0.9 °/step	0.22 °/step	396 °/sec	11 °/sec	360 °
tilt stage	0.9 °/step	0.018 °/step	32.4 °/sec	0.9 °/sec	360 °

Table 7. Specifications for the components of the 5-motion-axes micro-CNC stage.

The side view, in Figure 24c, shows the macro-Z motion stage, which is designed to translate the entire micro-CNC stage in the longitudinal direction. The macro-Z motion stage is required for the specimens at various heights, and is driven by a DC motor with a large translation limit of 18 cm.

The specifications for the motion axes of the micro-CNC stage are listed in Table 7. All stepper motors in the micro-CNC stage have the bipolar configuration, and are capable of operating in half-stepping mode [62]. The spatial resolution for the two dimensional patterning, for which the X and Y motion stages are used, is 4 μ m for the MP-I system. The minimum speed is the lowest speed for the continuous movement of the stages. The minimum continuous speeds are important to engrave continuum linear features using the pulsed irradiation from the excimer laser. The size of the two-dimensional patterning is limited to $13 \times 13 \text{ mm}^2$ because of the translation limits of the X and Y motion stages. The rotation and tilt stages are designed to have 360° turns. The specification of the micro-CNC stage is one of the most important criteria that have to be considered for designing patterns on the CVD diamond films.
Chapter IV

LASER-DIAMOND COUPLING

4.1. Laser-Diamond Interaction

4.1.1. Excimer laser irradiation on CVD diamond film

Typical UV-lasers make use of stimulated emission from excited molecular gases, such as ArF, KrF, XeCl, or XeF. Pulsed output of the lasers has a wavelength range from 193 nm to 351 nm, and duration time range from 10 ns to 30 ns. Due to the characteristics of UV-lasers (i.e., short radiation wave length and rapid pulse duration time), large amount of radiation energy can be transferred in a thin layer of a target surface. When the laser irradiance, defined by Watt/cm², exceeds an inherited threshold value of the target material, a thin layer is instantaneously evaporated by breaking atomic bonds upon the irradiation [63-67]. Upon the ablation process, most of the absorbed energies are used up for the sublimation of exposed atoms within tens of nanosecond range. This causes localized ablation only where the photon energies are absorbed. The selective ablation makes precision micromachining possible by imaging a desired pattern on a target. The laser in the setup is the KrF excimer laser (Lambda Physik®, model COMPex 301) with a wavelength of 248 nm, a rectangular pulsed beam of 1.3×3.0 cm² in TEM00 mode, a maximum pulse energy of 1.5 J and a maximum repetition rate of 10 Hz.



Figure 25. Schematic diagram of the excimer laser setup for the laser-diamond interaction.

Excimer laser setup used for the laser-diamond interaction is shown in Figure 25. Since the imaging system follows the thin lens principles of optics, the imaging plane is determined by the focal length of the convex lenses and the distance between the mask and the convex lenses [61]. A target surface is placed at the imaging plane where the demagnified pin-hole mask (1 mm diameter) is sharply focused for the ablation process. The imaging system is composed of a x-y-z specimen stage, two planar convex lenses (f = 295 mm and f = 101 mm, respectively) and a dielectric reflector (more than 99.5 % reflectivity). Two guiding lasers are used to aid focusing of the excimer laser imaging system. The crossover point of the two visible guiding lasers marks the imaging plane of the system.



Figure 26. Surface morphology of as-synthesized CVD diamond film subjected the laserdiamond interaction.

Figure 26 show the as-synthesized diamond film used in this preliminary laserdiamond interaction experiments. The surface morphology of the diamond thin film shows the fully faceted 3-D diamond crystals, with stacking-fault reentrant grooves [4]. The polycrystalline diamond film (AT109) was hetero-epitaxially grown on a single crystal silicon wafer, and has an average grain size and thickness of 2 μ m and 7 μ m, respectively. The diamond film was subjected under three different processing environments, such as the ambient air, the vacuum condition and the gas-streaming condition. Figure 27 shows the schematic diagrams for the processing environments.



Figure 27. The schematic diagram showing irradiation conditions in; a) the ambient air, b) the vacuum condition, and c) the gas-streaming condition.

The interaction, between the CVD diamond and excimer laser pulses, showed drastic changes among the different processing environments. The film was subjected under the same irradiation conditions, in which the laser irradiance, repetition rate and number of pulses were fixed at 4×10^8 W/cm², 1 Hz, and 20 times, respectively. A circular beam spot (145 µm diameter) was illuminated on the film surface by the pin-hole mask in the imaging system.

4.1.2. Irradiation in ambient air

Series of SEM micrographs in Figure 28 are taken from the irradiation in the ambient air, which is under stationary air in ambient atmosphere. In the ambient air, the ablation-debris deposition is observed that the edges are spoiled by the accumulation of the ejection. In this process, the pulsed irradiation eradicated the diamond film, and revealed the silicon substrate of the ruffled crater. In Figure 28a, the circular spot at the center was irradiated under previously described imaging system. The diamond surface around the irradiated spot show distinctive plasma affected zone (PAZ), which has somewhat symmetrical, ring-shaped patterns with spikes. The areas of PAZ indicated by 1, 2, and 3 in Figure 28a are magnified and observed in Figure 28a-1, 3a-2 and 3a-3, respectively. In Figure 28a-1, the area near the edge of the spot has suffered from heavy deposition of debris and damage on diamond crystals. The deposition is gradually reduced in Figure 28a-2 and 3a-3 as the distance increases from the spot. The debris and deposition of the ejected materials are observed at distances up to 10 times the spot diameter (145 μ m). The PAZ is caused by combination of deposition of ablation debris and thermal damage upon the expansion of high temperature plasma. Figure 28a-3 shows the debris in irregular shapes, which were ejected from the diamond film and substrate material. The temperatures of ablation-induced plasma have been measured around $10^3 \sim 10^4$ K from irradiation on graphite targets [68-70]. The temperature distribution, around the irradiated spot, is assumed to have an exponential decay type of radial distribution, dispersed due to the formation of the plasma [66]. From Figure 28b, it is obvious that the material ejection and redeposition occurred around the spot. The irradiated spot appears to be a crater, which has ruffled bottom from the surface melting. In this process, the pulsed irradiation eradicated the diamond film, and revealed the silicon substrate of the ruffled bottom. In Figure 28c, the crater is tilted and observed in SEM. Uneven depths of the crater were observed. The deep and ruffled crater indicates the melting of the silicon substrates, and the edges of the spot are piled up with injected materials.

A part of the spot edges is magnified in Figure 29. The radial-symmetric liquid ejection from the silicon substrate damaged the diamond film layer around the spot edges due to high temperature instability of the synthesized diamonds [3-5, 58]. Inside the piled up edges, the crater has bumpy structure with small wavelets as indicated by an arrow.



Figure 28. SEM micrographs showing excimer laser irradiation in the ambient air; a) the irradiation spot and surrounding with distinctive PAZ marked by 1, 2, and 3, b) the irradiation spot, c) highly tilted (75°) image for the irradiation spot, a-1) magnified view of zone 1 from the figure a, a-2) magnified view of zone 2 from the figure a, a-3) magnified view of zone 3 from the figure a.



Figure 29. Edge of the irradiation spot in the ambient air showing the radial-symmetric ejection and damage near the edges.

The wavelets are formed by the surface convection of the substrate and the propagation of stress waves upon expansion of high temperature plasma [26, 66]. During the short dwelling time (25 ns) of the excimer laser pulse on the film surface, atomic or molecular bonds of the material are broken due to the transmission of high-energy irradiance from the laser pulse. After the short interaction, disintegrated atoms and molecules are released from the surface, forming a plasma due to their high-energy states. The surface of the irradiated spot is heated by the high temperature plasma, which results in melting, oxidation, and other thermal reactions. The thermal expansion of the high temperature plasma induces propagation of stress waves, resulting the ejection of debris and deposition of debris around the irradiated spot.

4.1.3. Irradiation in vacuum condition

A vacuum chamber was constructed to examine the laser interaction in vacuum. A schematic diagram in Figure 27 shows the vacuum chamber, with quartz window for transmitting excimer laser pulse, and an additional window for the focus-guiding laser. Using a rotary-vane vacuum pump, a low vacuum condition (10.2 KPa) was gained in the chamber. The vacuum chamber was placed on the x-y-z stage of the imaging system. Series of SEM micrographs in Figure 30 are taken from the irradiation under vacuum condition. In Figure 30a, the PAZ, around circular spot at the center, was considerably reduced as compared to the Figure 28a in atmospheric environment. However, in Figure 30b, surrounding around the irradiated spot still show the PAZ. Even though the material ejection from the silicon substrate was not observed in this condition, the edges of the spot are blurred and spoiled by the plasma damage. The areas around the PAZ, indicated by 1, 2, and 3, are magnified and observed in Figure 30b-1, 6b-2 and 6b-3, respectively. In Figure 30b-1, the edge of the spot did not show the ejection of the silicon substrate, however, droplet-like precipitates are observed near the crater. In Figure 30b-2, significant amounts of the droplets are extensively observed in the PAZ. In Figure 30b-3, the damages on the diamond film appear somewhat different from those of the inside. In Figure 30c, the tilted image shows that the surface of the crater is relatively even. No melting of the silicon substrate is also observed at the spot, however, the blurred spoiled are prominent.



Figure 30. SEM micrographs showing excimer laser irradiation in the vacuum condition; a) the irradiation spot and surrounding, b) the irradiation spot with distinctive zones marked by 1, 2, and 3, c) highly tilted (75°) image for the irradiation spot, b-1) magnified view of zone 1 from the figure b, b-2) magnified view of zone 2 from the figure b, b-3) magnified view of zone 3 from the figure b.



Figure 31. Near spot edge area showing the plasma affected zone in the vacuum condition.

The PAZ near the spot edge is shown in Figure 31, in which the debris shows both the droplet-type deposition, and spread-type deposition.

In Figure 32, the part of the PAZ is magnified to show that the droplets are formed out of the spread-type debris deposition of the diamond film. As the number of laser pulse increases to ablate the film surface, more carbon debris are deposited near the irradiation spot, where the diamond crystals are suffering intense heating from the expanding plasma. The accumulated debris are affected by the heat and shock wave from the plasma, and formed droplets due to their high surface tension. Rapid solidification follows after the plasma is dissipated in the chamber.



Figure 32. Plasma affected zone in the vacuum condition showing the formation of the debris droplets.

The dispersion of the plasma is faster in the low-pressurized medium [71]. Even though some damage was found in the wake of expanding plasma, the area near the irradiation spot showed the reduced PAZ, due to the rapid dispersion of the plasma. The vacuum condition showed quite different morphology of the PAZ due to the lack of oxygen or other reactive gases.

4.1.4. Irradiation in gas-streaming condition

In the gas-streaming condition, a single nozzle was installed to blow a 99.9 % argon gas over the surface of the diamond thin film, upon the laser pulse irradiation. To blow an inert gas, the nozzle was positioned about 3 cm from the irradiated spot and 30°

degrees to the film surface. Diameter of the nozzle was 2 mm and the argon gas flow rate was 5×10^{-4} m³/sec.

A series of SEM micrographs in Figure 33 are taken from the irradiation in gasstream condition. In Figure 33a, no plasma affected zone was observed around the circular spot at the center, in contrast to the cases in the ambient air and the vacuum conditions. In Figure 33b, areas near the irradiated spot show no visible damage, however, a close observation revealed slight imperfections along the direction (arrows) of the gas stream. The arrows indicate the direction of the argon gas stream, which gives rise to the regional differences, marked by 1, 2 and 3 on the micrograph. The areas indicated by 1, 2, and 3 are magnified and observed in Figure 33b-1, 9b-2 and 9b-3, respectively. Since the argon gas stream passes from area 1 to area 2, the area 1 in Figure 33b-1 shows intact diamond crystals. In contrast, area 2 in Figure 33b-2 shows light damage on the crystal surface. The light damage was caused by the bent plasma, which was blown by the gas stream. The wake of the bent plasma causes light damages in near edge area as show in Figure 33b-3. In Figure 33c, the crater is observed by a high-angletilting in SEM. The crater shows the flattest surface among the processing conditions. The irradiated spot shows sharp and clean edges throughout all micrographs in Figure 33. In Figure 34, partially ablated diamond crystals are shown at the edge of the spot. The laser-sectioned crystals, in sizes of 2 μ m ~ 5 μ m, retain their original appearances, which show the feasibility of the micromachining in micron and sub-micron range. One of the slightly damaged diamond crystals is magnified in Figure 35, which shows light deposition of the ablation-debris on the edges and corners of the crystal.



Figure 33. SEM micrographs showing excimer laser irradiation in the argon gasstreaming condition, a) the irradiation spot and surrounding, b) the irradiation spot with areas marked by 1, 2, and 3, arrows indicate gas stream direction, c) highly tilted (75°) image for the irradiation spot, b-1) magnified view of area 1 from the figure b, b-2) magnified view of area 2 from the figure b, b-3) magnified view of area 3 from the figure b.



Figure 34. Edge of the irradiation spot showing ablation-sectioned diamond crystals in the argon gas streaming condition.



Figure 35. Light deposition of the ablation-debris on the edges and corners of the diamond crystal in the argon gas streaming condition.



Figure 36. Surface topographies of the irradiation spots of the diamond film in the different processing environments; a) ambient air, b) vacuum condition, and c) argon gas-streaming condition. The topographies were taken by a confocal laser scanning microscopy.

Surface topographies of the irradiated diamond film are compared in Figure 36.

The topographic depth profiles were obtained by the confocal laser scanning microscope.

In Figure 36a, the ambient air exhibits the deepest average crater depth (12 μ m) with the

most uneven crater surface. It also shows the severe damages at the spot edges and surrounding. The surface roughness was improved under the vacuum condition, as shown in Figure 36b. Accordingly, the average crater depth is reduced to $5.5 \mu m$. However, the blurred spot edges are extensively observed due to the plasma damages. In Figure 36c, the gas-stream condition shows the most optimum irradiation on the diamond film. Measured average crater depth is $4.5 \mu m$. The sharp spot edges and even crater surfaces are remarkable in the image.

When the argon gas stream is passing over the irradiated spot, it dissipates the high temperature plasma off from the surface, reducing the plasma-material interaction. The gas steaming not only blows the ablated particles away, but also effectively quenches the surrounding. Even though the slight imperfections were found in some portions of the near-edge areas, overall feasibility of the gas-stream condition is good for the micromachining of diamond films.

Based on the observed gas-streaming effects, the gas delivery unit in the MP-I system was designed. The gas delivery unit has three nozzles in a triangular geometry, which can prevent the plasma bending and following imperfections in the single nozzle streaming. Details are discussed in Chapter 2. With the three-nozzle gas delivery, helium gas was also considered for the inert gas-streaming in further studies in later chapters. However, the vacuum condition was excluded due to the complexity caused by the vacuum chamber and the limitation on the target translation for the 3D structuring.

4.2. Parameters of Laser-Diamond Coupling

4.2.1. Excimer laser ablation rate of CVD diamond films

The ablation by pulsed lasers depends on laser wavelength, laser irradiance and absorptivity of the target material. The absorptivity is a material constant, which depends on the material properties, such as heat capacity, latent heat of evaporation, thermal conductivity and density [14]. The ablation rate is an important parameter to predict depth or mass removal rate for the pulsed laser-based micromachining.

4.2.1-a. Experimental setup for the rate measurements

The ablation rate of the CVD diamond film was obtained by measuring the ablation depth as a function of the number of laser pulses and the laser irradiance. The measured ablation rates were compared among the gas processing conditions, such as the ambient air, helium gas-streaming and argon gas-streaming. Figure 25 shows the schematic diagram of the excimer laser setup for the rate measurements. The laser used in the system is the KrF excimer laser (Lambda Physik[®], model COMPex 301) with a wavelength of 248 nm, a rectangular pulsed beam of $1.3 \times 3.0 \text{ cm}^2$ in TEM₀₀ mode, a maximum pulse energy of 1.5 J and a maximum repetition rate of 10 Hz. The rectangular pulsed laser beam from the resonance passes through the 2.2 mm pin-hole aperture, and then the circular beam is focused by two planar convex lenses in focal lengths 295 mm and 50 mm, respectively.



Figure 37. Schematic diagram of the excimer laser setup for the ablation measurements.

The focused spot size on the diamond films was 175 μ m. Three gas nozzles are installed around the objective lens to deliver dynamic gas streaming over the irradiation spot. The nozzles are positioned about 3 mm from the irradiation spot and 30° degrees to the film surface. The diameter of gas nozzle is 2 mm and the gas flow rate is held constant at 5×10^4 m³/sec. Details about the three-nozzle gas delivery unit are discussed in Chapter 3. The diamond films used in this investigation were hetero-epitaxially grown, on single crystal silicon wafers, by the microwave plasma assisted CVD. The average grain size and vertical thickness of the diamond films were 10 μ m and 35 μ m, respectively. The diamond film was subjected to the three gas processing environments, such as ambient air, helium gas-streaming and argon gas-streaming. The average ablation depth was measured by the confocal laser scanning microscope (LSM), Zeiss 210, using the optical z-sectioning. The confocal images were taken from all irradiation spots under various processing conditions, and then linear profiles of the spots were recorded. Figure 38 shows examples of the scanned images from an irradiation spot for the depth profile. The confocal image of the irradiation spot is shown in Figure 38a, and its linear depth profiles are shown in Figure 38b and c. The linear profiles were compared with the topographic depth profiles for average values. The topographic depth profiles were obtained by the optical z-sectioning of the surface topography. An example of the series of the topographically z-sectioned images from an irradiation spot is shown in Figure 39, in which the bright areas indicate the image planes in focus with the listed depth values.

4.2.1-b. Ablation rate of CVD diamond film

The diamond surface was irradiated up to 200 laser pulses to measure the ablation rate as a function of the number of laser pulses. The pulse repetition depth and the laser irradiance were held constant at 2 Hz and 6×10^8 W/cm², respectively. Figure 40 shows ablation depths as a function of number of laser pulses. The ablation rates are compared among the gas processing environments, such as ambient air, argon gas streaming and helium gas streaming. An approximately linear relationship was observed in the range monitored between the ablation depth and number of laser pulses. At the initial stage of the laser ablation, indicated by the arrow between 0 and 20 laser pulses, a slightly higher ablation rate is observed due to the rough surface morphology of the polycrystalline CVD diamond film.







(c) high-resolution profile

Figure 38. Depth profile measurements of the irradiation spot by the confocal laser scanning microscope; a) confocal image of the irradiation spot, b) linear depth profile across the spot from the inset b in the figure a, and c) high-resolution linear profile near the spot edge from the inset c in the figure a.



Figure 39. Topographic depth profile of the irradiation spot by optical z-sectioning of the surface topography.



Figure 40. Ablation depth as a function of the number of laser pulses on the CVD diamond film.



Figure 41. Ablation depth as a function of the laser irradiance on the CVD diamond film.

No significant difference was found on the ablation rate among the gas processing environments. The average ablation rate of 0.14 μ m/pulse was obtained from the linear relationship.

The ablation rate as a function of the laser irradiance was also measured by varying the laser energy fluence from 2.4×10^8 W/cm² to 8.4×10^8 W/cm², with a constant number of laser pulses at 200 times and a constant repetition rate at 2 Hz. The plot of the ablation depth versus the laser irradiance is shown in Figure 41. The monitored range of the laser energy fluence was set between the ablation threshold (~ 10^8 W/cm² [17, 18]) of diamond film and the maximum energy output of the laser irradiance is approximately linear in the range observed in this study. The gas processing environments did not significantly alter the ablation rate. The slope of the plot, ablation depth versus the laser

irradiance, represents the coefficient of laser energy absorption τ (cm³/W). This coefficient is a material constant, which depends on the physical properties of the material, such as heat capacity, latent heat of evaporation, thermal conductivity, density, and surface reflectivity [14]. The τ also indicates the volume removal rate, which is essential to the modeling of the ablation process.

4.2.1-c. Modeling for the depth ablation

In this study, the linearity found in the ablation depth versus the pulse numbers (Figure 40) and the laser irradiance (Figure 41) gives the relationship:

$$d = \tau \cdot n \cdot I \qquad \qquad \text{Equation 9}$$

where d is the ablation depth (μ m), τ is the coefficient of laser energy absorption (cm³/W), n is the number of laser pulses, and I is the laser irradiance (W/cm²). This equation assumes that the laser irradiance is steady through the ablation process; hence, the depth ablation rate stays constant. It also assumes that the linearity exists in the observed laser irradiance range, which is relatively small for the possible irradiance rages for the ablation of diamond films.

Even though the approximation of linearity was reasonable in the relatively small depth range observed in this study, the nonlinearity exists due to the divergence of the focused laser beam. When the divergence of the focused laser spot is taken into account, nonlinear relationship has to be considered for the ablation depth as a function of the number of laser pulses.



Figure 42. Schematic diagram for the laser irradiation with divergent laser beam.

Figure 42 shows the schematic illustration in which the laser irradiation with circular beam on a flat surface was supposed. The initial radius r_i at the initial target surface, *i.e.*, at the image plane, is diverged to the final radius r_f after the ablation depth *d*. The divergence angle α is the angle between the edge of the cone of the laser irradiation and the vertical at the center of the circular beam spot. The α is also known as the angle of the numerical aperture (*NA*), in which $NA = \eta \sin \alpha$ [72]. Where the η is the refractive index of the medium in which the light passes through, and $\eta = 1$ in the air. The numerical aperture in optics represents the light gathering power of a lens. From Figure 42, the relationship among the parameters can be written as:

$$\tan \alpha = \frac{r_i}{l} = \frac{r_f}{(l+d)}$$
 Equation 10

where the imaging distance l is the distance between the focal point of the lens and the image plane on the initial target surface. From this relationship, the final radius r_f can be written as:

$$r_f = r_i + \frac{r_i d}{l}$$
 Equation 11

Then, the area of diverged spot size πr_f^2 is:

$$\pi r_f^2 = \pi \left(r_i + \frac{r_i d}{l} \right)^2$$
$$= \left(\frac{\pi r_i^2}{l^2} \right) d^2 + \left(\frac{2\pi r_i^2}{l} \right) d + \pi r_i^2$$
Equation 12

Substitute the initial spot size πr_i^2 for A_i and express the diverged spot size as a function of ablation depth d:

$$A(d) = \left(\frac{A_i}{l^2}\right) d^2 + \left(\frac{2A_i}{l}\right) d + A_i$$
 Equation 13

where A(d) is the spot size as a function of the ablation depth d. The initial spot size A_i , and the imaging distance l are the processing constants. Equation 13 shows that the initial spot size A_i is gradually enlarged as the ablation depth d increases, and the size of the diverged spot A(d) is the second order polynomial function of the ablation depth d. Since the laser irradiance (W/cm²) is inversely proportional to the beam spot size, the depth dependent laser irradiance I(d) can be written as:

$$I(d) = \frac{W}{A(d)}$$
 Equation 14

From Equation 9, the ablation depth as a linear function of the number of laser pulses is:

$$n = \frac{d}{\tau \cdot I}$$
 Equation 15

For the nonlinear divergence compensation, the laser irradiance I in this linear relationship is substituted for the divergence dependent laser irradiance I(d). Accordingly, the combination between Equation 14 and Equation 15 gives the nonlinear, divergence compensated ablation depth as a function of the number of laser pulses:

$$n = \frac{d \cdot A(d)}{\tau \cdot W}$$
 Equation 16

Combining with Equation 13 and rearranging for d give the pulse number n as the third order polynomial function of the ablation depth d:

$$n = \left(\frac{A_i}{\tau \cdot W \cdot l^2}\right) d^3 + \left(\frac{2A_i}{\tau \cdot W \cdot l}\right) d^2 + \left(\frac{A_i}{\tau \cdot W}\right) d^4$$
$$= \frac{A_i}{\tau \cdot W} \left(\frac{d^3}{l^2} + \frac{2d^2}{l} + d\right)$$
$$= \frac{1}{\tau \cdot I_i} \left(\frac{d^3}{l^2} + \frac{2d^2}{l} + d\right)$$

Equation 17

where I_i is the initial laser irradiance from the relationship $I_i = W/A_i$. In Equation 17, the initial spot size A_i , imaging distance l and laser power W are the processing constants, which can be measured form the experimental setup for the laser irradiation. As discussed in Section 4.2.1-b, the coefficient of laser energy absorption τ is the material constant, and can be obtained from the slope of the plot of the ablation depth versus the numbers of the pulses and the laser irradiance.



Figure 43. Ablation depth d as a function of the number of laser pulses n according to the Equation 17.

With the measurable processing constants, the ablation depth can be predicted by the number of laser pulses in Equation 17. This equation accounts the divergence of the focused laser beam, which results in the nonlinear decrease in the laser irradiance. According to Equation 17, the ablation depth is shown as a function of the number of laser pulses in Figure 43. Due to the depth dependant laser irradiance I(d), gradual decrease in ablation rate $(\Delta d/\Delta n)$ is expected as the number of the laser pulses increases. The lower boundary of the plot is where n = d = 0, and upper boundary is the point where the depth dependent irradiance I(d) drops below the ablation threshold of the target material. In the ablation process with the same material and optics setup, *i.e.*, constant τ and l, the curvature of the line is mainly depends the initial irradiance I_i , as show in the graph.

divergence angle α	3° degree
initial spot size A_i	$2.40 \times 10^{-4} \text{ cm}^2$
imaging distance l	0.167 cm
absorption coefficient τ	$2.305 \times 10^{-14} \text{ cm}^3/\text{W}$
initial irradiance I_i	6×10 ⁸ W/cm ²

Table 8. Measured processing parameters for the nonlinear ablation depth modeling.

The ablation with higher initial laser irradiance reaches its upper boundary, *i.e.*, ablation threshold due to the beam divergence, faster than the ablation with lower initial laser irradiance.

4.2.1-d. Prediction of the ablation depth

The modeled equation for the nonlinear ablation rate is applied to the experimental data acquired in Section 4.2.1-b. The processing parameters were measured from the experimental setup in Section 4.2.1-a and the acquired data in Section 4.2.1-b. The measured processing parameters are shown in Table 8. Using these parameters, Figure 44 shows the modeling of the ablation depth as a function of the number of the laser pulses. Since the subjected diamond film has the small average thickness of 35 μ m, the prediction of the ablation depth was extended up to 1000 μ m by the modeling. The linear function was plotted based on Equation 9 and the nonlinear function was plotted based on Equation 4.2.1 and the ablation depth region less than ~ 50 μ m. In the small ablation depth range, the differences between the linear and nonlinear functions were less than ~ 5%.



Figure 44. Modeling of the ablation depth as a linear function of the number of the laser pulses, and as a nonlinear function of the number of the laser pulses (at the initial laser irradiance 6×10^8 W/cm²).

However, in the ablation depth range close to 1000 μ m for deep drilling or high aspect ratio micromachining, the required number of laser pulses is almost tripled in the nonlinear ablation depth prediction, as compared to that in the linear function. Similarly, the predicted ablation depth with 2×10^4 pulses is 2800 μ m for the linear function, but only 1000 μ m for the nonlinear function. The discrepancy between the linear and nonlinear functions is exponentially increased as the number of laser pulses increases.

The modeling for the divergence compensation showed that the approximation of the linearity in this study was reasonable in the range of the ablation depth less than ~ 50 μ m. In this range of ablation, no significant reduction of the ablation depth was expected due to the negligible divergence of the laser beam. The degree of the beam divergence, consequently the reduction in the depth ablation rate, mainly depends on the optical setup

of the ablation process. In optics, the larger value of NA results in the greater beam divergence [72]. In the optics setup in this study, we have chosen a small numerical aperture, $NA = 5.23 \times 10^{-2}$ ($\alpha = 3^{\circ}$). In the observed range of ablation depths up to ~35 µm in this study, the calculated loss of the laser energy is less than 2.5 % of the initial irradiance, which is insignificant to exhibit nonlinearity on the monitored range.

4.2.1-e. Verification of the modeling

The prediction of the ablation depth is essential for the precision micromachining, especially for the deep ablation for the high-aspect-ratio features. The proposed nonlinear modeling was verified by subjecting a thick diamond film for the ablation depth measurement. The thick CVD diamond film, average thickness 270 µm and average grain size 40 µm, was used to allow enough ablation depth for the deep ablation. The silicon wafer substrate, where the CVD diamond film was grown by the heteroepitaxial growth, was completely dissolved in the etching solution (50%HNO₃ + 25%HF + 25%CH₃COOH) to acquire a freestanding diamond film. The substrate side of the freestanding diamond film, which retained flatness similar to the polished silicon wafer, was exposed to the laser irradiation. The same experimental setup described in Section 4.2.1-a was used for the laser irradiation. The diamond surface was irradiated by up to 2000 laser pulses to measure the ablation depth as a function of the number of laser pulses. The pulse repetition rate and the laser irradiance were held constant at 10 Hz and 6×10^8 W/cm², respectively. For the modeling of the ablation process, the processing parameters were measured and tabulated in Table 9.

divergence angle α	3° degree
initial spot size A_i	$2.40 \times 10^{-4} \text{ cm}^2$
imaging distance l	0.167 cm
absorption coefficient $\boldsymbol{\tau}$	$2.661 \times 10^{-14} \text{ cm}^3/\text{W}$
initial irradiance I_i	$6 \times 10^8 \text{ W/cm}^2$

Table 9. Measured processing parameters for the nonlinear ablation depth modeling.

The measured absorption coefficient τ (2.661×10⁻¹⁴ cm³/W) was close to that of the other diamond (2.305×10⁻¹⁴ cm³/W) film measured in Table 8. Using these parameters, the linear function was modeled, based on Equation 9, and the nonlinear function was modeled based on Equation 17. Figure 45 shows the modeled linear, modeled nonlinear and experimentally measured ablation depths, which are plotted as a function of the number of laser pulses.

Unlike the laser irradiation on the rough polycrystalline diamond surface (see Figure 40), the irradiation on the flat surface of the freestanding diamond film did not exhibit the high initial ablation rate. In the measured ablation depth, the onset of the nonlinearity was observed near ~ 120 μ m by ~1000 number of pulsed irradiation. The trend line of the measured ablation depth showed slightly higher curvature than that of the modeled nonlinear ablation depth. The higher curvature in the plot results in the lower ablation depth at the same number of pulsed irradiation. The lower ablation depth from the experimentation might be due to the confinement of the laser-induced plasma in the deep-dilled holes.



Figure 45. Ablation depth as a function of the number of laser pulses on the thick diamond film.

In the laser ablation process, the laser-induced plasma contains the ablated carbon particles, which are ejected to the ambient together with the expanding plasma [27]. The trapped plasma in the deep-drilled hole causes the redeposition of the ablation particles in the hole. The redeposition reduces the depth ablation rate upon the laser irradiation.

4.2.2. Laser-diamond interaction

Carbon exists in a few solid-state phases in the atmospheric condition. Diamond and graphite are well-known solid-state phases. Diamond of sp^3 bonding is optically transparent, electrically insulating and chemically inert [73]. In contrast, graphite of sp^2 bonding is optically opaque, electrically conductive, and chemically reactive [41]. Application of heat and pressure transform the carbon phase between diamond and graphite.

The UV excimer lasers are suitable for the ablation processing of diamond films due to the high optical absorption in the UV range. The magnitude of the ablation is determined by the laser wavelength and irradiance, and the optical absorptivity and other properties of the target material [14, 74].

4.2.2-a. Diamond to graphite phase transformation

The phase transformation from diamond to graphite has been reported upon the irradiation by the various pulsed lasers on CVD diamond films [15, 16, 18, 21, 24, 75]. The diamond to graphite transformation was inevitable in the laser irradiation in this study, in which the KrF excimer laser with 248 nm wavelength and 25 ns pulse duration was source of the irradiation. Regardless of the gas processing conditions, the laser irradiation resulted in the diamond to graphite transformation on surface layers. The structural transformation was detected by extinction of the diamond spectrum in the Raman spectroscopy. A thick CVD diamond film, average thickness 110 μ m and average grain size 50 μ m, was subjected to 20 pulses of the laser irradiation with the laser irradiation with the laser

the monochromatic light source (Argon laser at 514.5 nm, 300 mW) was illuminated on the diamond film to detect the Raman peak shift. By comparing before and after the laser irradiation, Figure 46 shows the extinction of the diamond Raman spectrum (1332 cm⁻¹) by the structural transformation.

In the carbon phase diagram, the CVD diamond exists in the metastable state of the graphite region [3]. The CVD diamond surfaces are reconstructed to graphite at the temperature region over 900°C. The phase transformation was mainly caused by the heat and pressure, which are created by the absorption of the laser energy and propagation of the plasma-induced shock waves [16, 75]. The surface heating by the laser irradiation results in the surface reconstruction from sp^3 bonded metastable diamond to the sp^2 bonded stable graphite configuration [4].

The evidences of the laser-induced diamond-graphite transformation led to the close examination on the evolution of the polycrystalline diamond surface morphology upon the laser irradiation. The evolution of the surface morphology, at the initial stage of the laser-diamond interaction, was observed by the atomic force microscope (AFM), Digital Instrument Nanoscope IIIa in Tappingmode[®]. The thin diamond film (BW062) with a small grain size was selected for the AFM observation. The average grain size and vertical thickness of the subjected diamond film was 2 μ m and 4 μ m, respectively. The diamond film was irradiated by the laser irradiance of 4×10⁸ W/cm² with 1, 3, 6 and 10 laser pulses.



Figure 46. Extinction of the diamond Raman spectrum (1332 cm⁻¹) by the excimer laser irradiation; a) before the laser irradiation, b) after the laser irradiation, and c) Raman spectrum.
The same experimental setup described in Section 4.2.1-a was used for the laser irradiation. The spot size on the diamond surface was 80 μ m.

Figure 47 shows the evolution of the surface morphology by the laser-diamond interaction. In Figure 47a, the unexposed surface shows sharp edges of the truncated {100} diamond crystalline. In Figure 47b, a preferential interaction was observed in which the sharp edges of the crystalline were chipped off by the single-pulse irradiation. After 3 pulses of irradiation in Figure 47c, the surfaces of the diamond crystals started to erode away. The sharp edges and vertexes of the diamond crystals were smoothened out by the laser irradiation. In Figure 47d and e, the surface morphology kept evolving in such a way as to gradually smoothen out the edges and vertexes.

The magnified view of Figure 47 is shown in Figure 48, which shows the submicron features of the surface morphology. The preferential diamond-laser interaction was noticed in Figure 48b that the edge of the diamond crystal (indicated by the arrow) was chipped-off by the laser irradiation. In Figure 48c, the evolution of the surface morphology was continued, not by the preferential edge chipping-off mechanism but by an overall smoothening-out mechanism. The significantly smoothened surface is observed after 10 times of the pulsed irradiation in Figure 48e.

From the observations in Figure 47 and Figure 48, it can be speculated that the preferential interaction by the edge-chipping-off mechanism occurs at the very initial stage with in 1 to 2 laser pulses. Then, the successive laser irradiation reduces the surface roughness in overall smoothening-out mechanism. The preferential laser-diamond interaction was observed in other type of the diamond crystals as well.



Figure 47. AFM (Tappingmode[®]) observation on the evolution of surface morphology by the excimer laser irradiation.



Figure 48. AFM (Tappingmode[®]) observation, in sub-micron scale, on the evolution of surface morphology by the excimer laser irradiation.



Figure 49. Observation of the Raman spectrum on the excimer laser irradiated diamond surfaces.

The observation of the Raman spectrum is shown in Figure 49 for the laser irradiated diamond surfaces. The single pulse irradiation in Figure 48b still exhibited some extent of the diamond spectrum, indicating that the surface was not entirely graphitized. Over 3 pulses of the laser irradiation, the surface completely lost the diamond spectrum. Hence, it is conclusive that the laser-diamond interaction causes the formation of an opaque graphitized surface layer within few pulsed irradiations. Then, the self-sustaining graphite layer absorbs the successive laser pulses, and the surface morphology evolves according to the ablation [18].

4.2.2-b. Evolution of surface morphology

To examine the evolution of the surface morphology beyond the initial interaction, a set of *in-situ* observations were performed on the CVD diamond film. The ESEM (Philips Electroscan 2020) was used for the *in-situ* observation of the evolution of the surface morphology. The acceleration voltage used in ESEM was 20 kV. The thick diamond film (thickness: ~ 110 μ m) with large grain size (average grain size: ~ 50 μ m) was selected for the macroscopic observation. The diamond film was irradiated by the laser irradiance of 6×10^8 W/cm² with 5, 20, 50, 100 and 200 laser pulses.

Figure 50 shows the macroscopic evolution of the surface morphology upon the laser irradiation. The arrows in Figure 50 indicate the same location through out the gradual exposures to the laser irradiation. After 5 times of the laser pulses in Figure 50b, the sharp edges of the diamond crystals are lightly etched by the irradiation. In Figure 50c and d, the edges and vertexes of the diamond crystals are gradually smoothened out, as the pulsed irradiation increased to 20 and 50 times. In Figure 50e, the uneven etching on the diamond surface significantly diminished the outlines of its original morphology. The rough surface in Figure 50a is entirely smoothened out in Figure 50f by 200 laser pulses. Figure 51 also shows the roughness reduction in larger area after 200 laser pulses. As shown in Figure 50b ~ e, the *in-situ* observation revealed that the roughness reduction occurred by the uneven etching of the crystalline surface.



Figure 50. ESEM *in-situ* observation on the evolution of the surface morphology of the laser irradiated diamond surface; a) 0 pulse, b) 5 pulses, c) 20 pulses, d) 50 pulses, e) 100 pulses, and f) 200 pulses. The arrows indicate the same position throughout the observation.



Figure 51. Roughness reduction of the polycrystalline diamond surface by the excimer laser irradiation; a) before the laser irradiation, and b) after 200 laser pulses at 6×10⁸ W/cm².

The sharp edges and vertexes exhibited higher etching rate than that the planes and valleys. The uneven etching ratio can be qualitatively explained by the overheating of the crystal edges and vertexes. Upon the laser irradiation, the absorbed laser energy heats the surface. The spread of heat is uneven when the target surface is rough. The protruded features such as edges and vertexes are overheated by the uneven spread of the heat [18]. The vapor screening by the laser-induced plasma also promotes the overheating of the surface features. The laser-diamond interaction causes, within few pulses, the formation of the self-sustaining amorphous graphite micro-layer. In Figure 52, the cross sectional view of the diamond film shows the formation of the graphite micro-layer. The self-sustaining graphite layer absorbs the energy from following laser irradiations, and determines the evolution of the morphology by the uneven etching on the surface.



Figure 52. Formation of the self-sustaining graphite micro-layer upon the excimer laser irradiation by 200 pulses of irradiation at 6×10⁸ W/cm².

4.2.2-c. Removal of graphite layer

To examine the environmental effects of the laser irradiation, the diamond film was subjected to the three different gas-processing conditions, such as ambient air, helium gas-streaming, and argon gas-streaming. The average grain size and vertical thickness of the diamond films were 10 μ m and 30 μ m, respectively. The laser irradiance, repetition rate, number of pulses, and gas flow rate were fixed at 6×10⁸ W/cm², 2 Hz, 200 times and 5×10⁴ m³/sec, respectively. A circular beam spot of 175 μ m in diameter was illuminated on the film surface by the excimer laser imaging system. The rapid transmission of high laser energy fluence causes disintegration of atomic bonds of the CVD diamond. After the short interaction, disintegrated atoms are released from the surface, forming plasma due to their high-energy states [16]. This results in deposition of debris around the irradiated spot, and the explosive expansion of the plasma induces the propagation of stress waves [27]. The ESEM was used to observe surface morphologies of nonconductive CVD diamonds. Regardless of the gas processing conditions, the laser irradiation resulted in the formation of the amorphous graphite micro-layer on the surface. However, the interaction between the CVD diamond and the excimer laser pulses showed quantitatively and morphologically different deposition of ablation debris among the gas processing environments.

The group of micrographs in Figure 53 shows the film morphology around the irradiation spot. All processing environments show deposition of carbon debris, which forms distinctive plasma affected zone (PAZ), around the irradiation spot. Near the spot edges, the largest amount of debris deposition is observed with argon streaming in Figure 53c-1, while the ambient air shows the least amount of deposition indicated in Figure 53a-1. The morphologies of deposited carbon debris are also different among the processing conditions. The origins for the quantitative and morphological differences of the carbon debris are discussed in Chapter 5. The graphite layers and deposited particles are chemically removed by boiling (~ 200°C) in 1:1 solution of CrO_3 and H_2SO_4 for 2 minutes. The solution is known for its dissolving ability of graphite [75]. After the cleaning, the irradiation spots are observed in Figure 53a-2, b-2 and c-2. In these figures, no visible residue of deposited carbon debris was found in all processing conditions. The helium gas-streaming (Figure 53b-2) and argon gas-streaming (Figure 53c-2) show no obvious damage around their spot edges. In contrast, light damage is found around the irradiation spot in the ambient air (Figure 53a-2).



Figure 53. Edges of the irradiation spots showing the carbon debris deposited by the irradiation (left column) and cleaned edges by the removal of the deposition (right column); a-1) ambient air - as irradiated, a-2) ambient air - after the cleaning; b-1) helium streaming - as irradiated, b-2) helium streaming - after the cleaning; c-1) argon streaming - as irradiated, c-2) argon streaming - after the cleaning.



Figure 54. Damaged diamond crystals around the spot edge from the laser irradiation in the ambient air; a) the damaged spot edge, the arrows indicate the damaged area, b) magnified view of the damaged area, indicated by the arrows.

Figure 54 shows the damaged diamond crystals around the spot edge, which is formed by the laser irradiation in the ambient air. The arrows in Figure 54a indicate the extent of damaged area near the irradiation spot. The damaged diamond crystals are magnified in Figure 54b, and the arrows also indicate the extent of the damaged area. The light damage, around the irradiation spot in the ambient air, can be explained by the plasmadiamond interaction, which results in over heating of area near the spot edge. In helium gas-streaming and argon gas-streaming conditions, the dynamic streaming upon the laser irradiation reduces the plasma-diamond interaction, resulting in intact diamond crystals near the spot edge.

4.3. Chapter Summary

The laser-diamond interaction was examined by subjecting the diamond film under three different processing environments, such as the ambient air, the vacuum condition and the gas-streaming condition. The interaction, between the CVD diamond and the excimer laser pulses, showed drastic changes among the different processing environments. The vacuum condition was ruled out due to the complexity caused by the vacuum chamber and the limitation of the target translation in the chamber. By the dissipation of the high temperature plasma off from the surface, the inert gas-streaming showed a good feasibility for the precise micromachining of diamond films. The gas delivery unit, which has three nozzles in triangular geometry, was designed based on the observed gas-streaming effects. With this gas delivery unit, further studies of the laserdiamond interaction were performed in the ambient air, helium gas streaming and argon gas streaming conditions.

The ablation rate of the CVD diamond film was obtained by measuring the ablation depth as a function of the number of laser pulses and the laser irradiance. The measured ablation rates were compared among the gas processing conditions, such as the ambient air, helium gas and argon gas, respectively. No significant difference was found on the ablation rate among the gas processing environments. Approximately a linear relationship was observed between the ablation depth and the number of laser pulses, and between the ablation depth and the laser irradiance. Based on these observations, linear and nonlinear models for the ablation process were proposed. The nonlinear model accounted for the divergence of the focused laser beam, and resultant decrease in the

laser irradiance. The nonlinear modeling proposed the number of the laser pulses as the third order polynomial function of the ablation depth. The nonlinear model was verified by the ablation on thick diamond film. The experimentally measured ablation depth showed slightly higher curvature than that of the modeled nonlinear ablation depth. The origin of the discrepancy is assumed to be due to the trapped plasma in the deep-drilled hole, which causes the redeposition of the ablation particles in the hole. The redeposition made the experimental rate of depth ablation lower than the expected ablation rate from the nonlinear modeling.

The initial stage of the laser-diamond interaction was observed by the AFM and Raman spectroscopy. It could be speculated from the AFM observation that the preferential interaction by the edge-chipping-off mechanism occurs at the very initial stage with in 1 to 2 laser pulses. Then, the successive laser irradiation reduces the surface roughness in overall smoothening-out mechanism. It was reasonably conclusive from the Raman spectroscopy observation that the laser-diamond interaction causes the formation of the graphitized surface micro-layer within a few pulsed irradiations. Then, the selfsustaining graphite layer absorbs the successive laser pulses for the ablation, and the surface morphology evolves according to the ablation.

To examine the evolution of the surface morphology beyond the initial interaction, *in-situ* observation was performed for the laser irradiation on the CVD diamond film. The sharp edges and vertexes exhibited higher etching rate than the planes and valleys. The roughness reduction was caused by the uneven etching on the jagged polycrystalline diamond crystals. The uneven etching ratio is explained by the overheating of the crystal edges and vertices due to the laser irradiation.

The removal of the graphite layers, and deposited particles were performed by boiling the sample in the mixed solution of CrO_3 and H_2SO_4 . for 2 minutes. No visible residue of deposited carbon debris was found after this chemical cleaning. The helium gas-streaming and argon gas-streaming show no obvious damage around their spot edges. In contrast, light damage is found around the irradiation spot in the ambient air.

Chapter V

LASER-INDUCED PLASMA ON CVD DIAMOND FILMS

5.1. Laser-Induced Breakdown Spectroscopy (LIBS)

5.1.1. Introduction to LIBS

Laser-induced breakdown spectroscopy is elemental analysis based on emission spectra from plasma, generated by a powerful laser pulse on a sample. The laser-induced breakdown spectrometry (LIBS) makes use of principles similar to those of conventional plasma atomic emission spectrometry, in which the plasma is induced by various ways, such as induction coupling, microwave, direct current, arc and spark [74, 76-81]. In conventional atomic emission spectrometry, the spectral emission is obtained by transportation of a sample to a plasma source for excitation. Consequently, sample preparation and complex design of an excitation chamber are required in most cases. In contrast, the LIBS utilizes pulsed laser ablation by optical radiation, which generates the laser-induced plasma directly from the sample. This direct ablation makes *in-situ* observation possible on emission spectra of gaseous, liquid, and solid samples without the sample preparation [74, 82]. The direct observation of laser-induced plasma in LIBS offers *in-situ* analyses on emission spectra of CVD diamond films in various gas processing environments.

5.1.1-a. Generation of laser-induced plasma

Laser-induced breakdown is defined as the generation of a practically totally ionized gas, *i.e.* the plasma, at the end of pulsed laser irradiation [74, 78, 82, 83]. The laser-induced plasma is formed when the laser energy irradiance exceeds the breakdown threshold of a target material, where the irradiance is determined by laser power per unit area (W/cm²). The laser-induced plasma is developed by the inverse bremsstrahlung absorption, during collisions among vaporized atoms, ions, and electrons. The inverse bremsstrahlung process is reverse of the bremsstrahlung process in which high-energy electrons emit electromagnetic radiation as they slow down in media [74, 76, 78, 82-86]. In the bremsstrahlung process, accelerated electrons lose energy by elastic and inelastic collisions with atoms and molecules. In the laser-induced plasma, electrons gain energy much larger than that of ionization, when the laser energy irradiance is high enough. The electrons in high-energy state generate new electrons by ionizing collisions. In spite of the collisions, some of the new electrons retain energy over ionization, thereby leading to cascade growth, the inverse bremsstrahlung process.

There are two main mechanisms for electron generation and growth by the inverse bremsstrahlung [74, 78, 82, 83, 87]. The first mechanism, called cascade ionization, is associated with absorption of laser radiation by electrons that collide with neutrals. When the electrons gain sufficient energy, they can ionize the gas or solid neutrals through the reaction,

$$e^- + M \rightarrow 2e^- + M^+$$
 Equation 18

where, e is an electron, M is a neutral atom or molecule. This reaction leads to the cascade breakdown, where the electron concentration increases exponentially with time. The cascade breakdown requires existence of initial electrons at the laser irradiation to gain excitation energy greater than ionization energy. Multiphoton ionization is the second mechanism, which involves the simultaneous absorption of ionization energy from a sufficient number of photons. The multiphoton ionization is described by the reaction,

$$M + nhv \rightarrow M^+ + e^-$$
 Equation 19

where *n* is number of photons, *h* is Plank's constant and *v* frequency. The ionization rate is proportional to the laser irradiance, and increases linearly with time. The multiphoton ionization is taken into account only when the incident laser pulse has a short wavelength less than about 1000 nm. For an example, the simultaneous absorption of more than 100 photons is required for the CO₂ laser ($\lambda = 10.6 \mu m$, hv = 0.11 eV) to ionize a carbon atom (ionization energy = 11.26 eV). In contrast, the KrF excimer laser ($\lambda = 248 nm$, hv =5.01 eV) requires only about 2 photons to ionize the carbon atom. Using the excimer laser of a short wavelength is far more probable for the ionization of the carbon.

The laser-induced plasma, especially for short wavelength lasers, is generated by combination of the two ionization mechanisms. The initial electrons are created by multiphoton ionization, and the initial electrons induce cascade ionization by the bremsstrahlung absorption.

5.1.1-b. Characteristics of Laser-induced plasma

The temporal evolution of the laser-induced plasma on a solid target is schematically illustrated in Figure 55 [18, 74, 82, 83, 88]. The diagram is based on 25 ns laser pulse duration for the KrF excimer laser and the laser irradiance over ablation threshold of a solid target.



Figure 55. Schematic diagram for the temporal evolution of the laser-induced plasma, illustrating various regimes of the emission spectra. 25 ns laser pulse duration of KrF excimer laser and irradiance over ablation threshold were assumed [18, 74, 82, 83, 88].

At the beginning of the '*laser pulse*' regime, the leading edge of a laser pulse starts to interact with the solid target. Consequently, the absorbed laser energy rapidly heats the surface layer to instantly vaporize the solid. During the heating of the surface layer, partial loss of the absorbed energy is caused by the latent heat of fusion and evaporation, and heat sink to the bulk by thermal conduction. The initial ionization is mainly achieved by the multiphoton absorption process [18, 83, 87], which release high-energy free electrons from the target surface. The early vapor-phase species interact with the trailing edge of the incident laser pulse and absorb up to 20% of energy from the laser pulse [88]. This interaction aids some internal ionization of the early vapor-phases. Collisions among the charged particles also lead to increase in temperature and pressure of the

initial plasma. However, absorption of the incident laser energy, which results in thermal ionization, is the main mechanism for the generation of initial plasma in the '*laser pulse*' regime. At the onset of the plasma, the emission spectra start to display continuum background, indicating the rapid heating.

In the 'ions' regime, the process of evaporation by the absorbed laser energy continues, and the electron density of the partially ionized vapor becomes high enough to propagate the inverse bremsstrahlung process. The ionization of the plasma is drastically increased by the onset of the inverse bremsstrahlung process, which exponentially increases the electron density of the plasma as a function of the time [78, 83-86]. The increased density of the excited electrons sharply elevates the plasma temperature. Multiply ionized, highly kinetic species are generated, and then these energetic particles expand ballistically to the ambient. Continuous growth and heating of the plasma at high temperature and high electron density make the plasma extremely high in energy density. The temperature of the plasma near the irradiation surface reaches to the order of 10^4 to 10^{5} [68-70, 89-91]. This causes the explosive expansion of the plasma, which sustains its luminosity up to 100 μ s in duration [27, 78, 83]. The electron density as well as the temperature sharply drops with the expansion of the plasma to the ambient. Until the plasma reaches its peak density and temperature, the inverse bremsstrahlung process continuously increases the continuum background of the spectral emission. When the plasma explosively expands, the recombination between multiply ionized particles and electrons forms the lower level ions, and the recombination releases continuum emission spectra [74, 78]. In the recombined ions, subsequent relaxation of the excited electrons to the ground state generates the characteristic ionic spectra [79, 92, 93].

In the 'atoms' and 'molecules' regimes, the expansion of the plasma causes continuous decrease in the electron density. The electrons lose their energy and recombine into ions to form neutral atoms and subsequent molecules. The valuable atomic and molecular emission spectra are obtained in theses regimes when the excited electrons of the neutral particles release their energy by returning to the ground state [93, 94]. The laser-induced plasma interacts with its surrounding during expansion [78]. The expansion of the high-pressure and high-temperature vapor drives shock waves into the target and atmosphere. As the radially expanding plasma sweeps across the target, thermal conduction and radiation across the thin boundary layer can transfer significant energy to the target surface.

5.1.2. LIBS instrumentation

The experimental setup for LIBS used in this study is shown in Figure 56. The laser in the LIBS is the KrF excimer laser (Lambda Physik[®], model COMPex 301) with a wavelength of 248 nm, a rectangular pulsed beam of 1.3×3.0 cm² in TEM₀₀ mode, a maximum pulse energy of 1.5 J and a maximum repetition rate of 10 Hz. The imaging optics setup includes an automatic aperture unit, a set of planar convex lenses (focal lengths 295 mm and 50 mm) and a focal point positioning unit. The focused spot size used in the LIBS is 650 μ m in diameter. Three gas nozzles are installed around the objective lens to deliver regulated dynamic gas-stream over the irradiation spot. The nozzles are positioned about 3 mm from the irradiated spot and 30° degrees to the film surface.



Figure 56. Schematic diagram of the LIBS setup for the acquisition of the laser-induced plasma on the CVD diamond film.

The diameter of the gas nozzle is 2 mm, and the maximum gas flow rate is 9.44×10^4 m³/sec. Helium and argon gases are used to dynamically alter the environment. Details of the excimer laser, imaging optics and the gas-streaming unit are discussed in Chapter 3.

Emission spectra of the laser-induced plasma were collected by the fused silica fiber optics, which has a range of wavelength transmittance from 240 nm to 2200 nm. Both ends of the fiber optics were polished with a series of diamond suspensions in particle sizes of 30 µm, 6 µm, and 1 µm. The colloidal silica, average particle size of $0.06 \,\mu\text{m}$, was used for the final step of the polishing. To collect the emission spectra, input end of fiber optics was installed at right angle to the incident laser beam, 5 mm from the center of the irradiation. The distance, between the fiber optics and the center of the laser irradiation, was kept to prevent deposition of ablation debris on the fiber optics, which resulted in drastic decrease in signal intensity. The fiber optics geometry in the system integrates spectral emission from the plasma, producing spatially averaged results in the spectrum. The output end of the fiber optics was placed in the monochrometer, Instrument SA, model HR-320. The monochrometer has the 0.32-meter coma corrected Czerny-Turner configuration [82], which includes a 147 grooves/mm grating with a reciprocal linear dispersion of 20.8 nm/mm. The primary function of the monochrometer is to isolate the wavelength of interest from other wavelengths. The isolated emission spectra were detected by a multi-channel CCD detector, EG&G PARC, model 1430P. The solid state CCD detector is composed of a matrix array of 576 columns by 384 horizontal tracks of charge-coupled pixels. When the matrix is exposed to a spectral source, photons strike the matrix generating electrical charge in the pixels. The charge in each pixel is amplified for analog signals, and then the analog signals are converted to 14-bit digital format in the CCD detector controller, EG&G PARC, model 1430-1. The digital signals are transferred to the OMA microcomputer, EG&G PARC, model 1460, for the signal processing.

In the LIBS in this study, the scanning range of wavelength was set from 350 nm to 825 nm. The intense reflection of the incident laser beam (248 nm) was screened by a

long-pass 350 nm optical filter. The resolution for the emission spectra, gained by the combination of the monochrometer and the detector, was 0.47 nm. The exposure time was set at 3 second, and the repetition rate of the excimer laser pulse was set at 10 Hz. By the exposure time and the repetition rate, the time-integrated emission signals for 30 successive laser irradiations were accumulated for each measurement. Emission lines from a mercury lamp [77], which show sharp and intense peaks in 200 nm to 600 nm wavelength region, were used for wavelength calibration of the emission spectra. To reduce the noise to the detector, all acquisitions of emission spectra were performed in a darkroom condition. The dark current of the detector was measured separately for each acquisition condition and subtracted for background correction of emission spectra.

A thick CVD diamond film (ST235), average thickness 110 μ m and average grain size 50 μ m, was used to allow enough ablation depth for the high-energy laser irradiation. The silicon wafer substrate, where the CVD diamond film was grown by the heteroepitaxial growth, was completely dissolved in the etching solution (50%HNO₃ + 25%HF + 25%CH₃COOH) to acquire a freestanding diamond film. The substrate side of the freestanding diamond film, which retained flatness similar to the polished silicon wafer, was exposed to the laser irradiation. The surface of the diamond film was carefully cleaned to prevent irrelevant spectra from organic contamination. To remove surface contamination, the surface of the diamond film was cleaned by ethanol in an ultrasonic cleaner, and exposed to 5 laser pulses prior to the acquisition. Each acquisition was taken on a fresh diamond surface for consistency.

5.1.3. Identification of line emission spectra

To examine the characteristics in emission spectra among the gas processing environments, emphasis was placed on observation of broad wavelength range, from 350 nm to 825 nm. Identification of the line emission spectra for the observed range was performed by comparing the acquired LIBS results to various standard sources. The standard atomic emission spectra from Notional Institute of Stand and Technology (NIST) were used for the identification of the line spectra from atoms and ions. The NIST has developed a computer software, *NIST Atomic Spectra Database* (NIST Standard Reference Database #78) [95]. This database can provide access and search capabilities for critically evaluated data on atomic energy levels, wavelengths, and transition probabilities. The molecular linear spectra were identified by tabulated molecular standard spectra [96]. Related investigations for LIBS, carbon emission spectra [68, 69, 89, 97-105], and ambient air breakdown [106, 107], were also referenced to verify the identification.

In Figure 57, the indexing maps display all probable atomic and molecular emission spectra with the emission spectra by LIBS on the diamond film. The line graphs show the emission spectra of the diamond film from the various gas processing conditions, and the bar graphs at the bottom show the standard emission spectra for the indexing. In the graphs, an arbitrary unit for the emission intensity was used for both the LIBS results and the standard spectra. The diamond emission spectra were obtained from the gas processing environments, such as ambient air, helium gas-stream and argon gasstream.



Figure 57. Indexing map for the emission spectra on the CVD diamond film, a) indexing map for the atomic emission spectra, b) indexing map for the molecular spectra.

The laser irradiance was 6.0×10^8 W/cm² for all conditions, and gas flow rate was 5×10^4 m³/sec for the helium and argon gases. Figure 57a shows the indexing map for the atomic emission spectra. For the atomic spectra from environmental gas breakdown, the collected data were compared with neutral and singly ionized standard emission spectra of oxygen, nitrogen, argon and helium. Higher levels of ionization of the environmental gases do not show significant contributions to the breakdown spectral emission [106, 107]. For the atomic emission spectra of the diamond, all ionization levels of the carbon (CI ~ CV) were compared to the collected spectra from the irradiation. Indexing map for the molecular emission spectra is shown in Figure 57b. All probable molecular emission systems of carbon, oxygen, and nitrogen are compared with the LIBS results from the various gas processing environments. Details of the molecular systems for the each element and identifications of the corresponding emission spectra are discussed in the following sections.

5.1.3-a. Identification of carbon emission spectra

Identification of carbon emission spectra is carried out by comparing collected emission spectra with both the band systems of molecular carbon emission spectra and individual emission spectra from carbon neutral and ions. In Figure 58, the emission spectra from the various gas processing environments are compared with the molecular carbon emission bands. The diatomic carbon emission bands and carbonitride emission bands were considered for the identification of the laser-induced plasma emission lines. The names, transitions and occurrences of the molecular emission bands are listed in Table 10.



Figure 58. Identification of molecular carbon emission spectra from the LIBS on CVD diamond film.

name of molecular spectra	transition	occurrence
C ₂ Swan system (first positive bands)	A ³ Π _g → X ³ Π _u	 direct excitation of C₂ molecules formation of excited state (d³Π_g) C₂ molecules via dissociation or recombination very frequent occurrence in sources containing carbon.
C ₂ High Pressure system	$A^{3}\Pi_{g} \rightarrow X^{3}\Pi_{u}$	• condensed discharge through CO at relatively high pressure
C ₂ Deslandres- d'Azambuja's system	$c \Pi_g \rightarrow b \Pi_u$	• condensed discharge through CO, CO ₂ , or C_2H_2
CN Violet system	$B^{2}\Sigma \rightarrow A^{3}\Pi$	 carbon plasma in air discharge tubes containing nitrogen and carbon
CN Red system	$A^{2}\Pi \rightarrow X^{2}\Sigma$	 introducing C₂H₂ and HCCl₃ into active nitrogen carbon arc in air discharge tubes containing nitrogen and carbon

Table 10. Molecular emission band systems for carbon and carbonitride [96, 100].

As shown in Figure 58, the intense C_2 Swan bands and CN Violet bands were observed in the collected spectral emissions. Weak signals of the both C_2 Deslandresd'Azambuja's system and C_2 High pressure system were identified as well. In contrast to the strong CN bands, no significant emissions for the CN red bands were identified. Figure 59 shows the comparison of the dominant molecular emission, CN Violet bands and C_2 Swan bands, among the gas processing conditions. The plasma emission spectra in ambient air exhibit very strong CN Violet bands and the lowest C_2 Swan bands. In contrast, the argon gas-streaming shows the strongest C_2 Swan band emissions with significantly reduced CN Violet bands. The helium gas processing condition shows the lowest CN Violet band emissions with higher C_2 Swan bands than those of ambient air.



Figure 59. Comparison of dominant molecular emission bands, CN violet and C_2 Swan, among the gas processing conditions.

Figure 60 shows identification of atomic carbon emission spectra from the laser-induced plasma on the CVD diamond film. Compared to the molecular spectra, relatively weak emission signals of the neutral carbon (CI) and the singly ionized atom (CII) were identified in Figure 60.



Figure 60. Identification of atomic carbon emission spectra from the LIBS on CVD diamond film.

Relative emission intensity, which is the ratio of a line spectrum to a continuum background, is compared among the gas processing conditions. The neutral atomic spectra of CI 447.18 nm, CI 538.03, and CI 711.32~711.98 nm exhibit no significant difference in relative intensity among the processing conditions. In contrast, the emission spectra of singly ionized atoms, CII 657.81 and CII 711.56~712.20, show a significant increase in relative intensities in helium gas processing conditions. The helium gas processing also developed additional singly ionized spectra at CII 723.13~723.64 nm.

5.1.3-b. Identification of environmental gas breakdown

The emission characteristics of the laser-induced plasma are largely influenced by the surrounding atmospheres. When the laser irradiance exceeds the energy threshold of ionization potential, the high-energy electrons in the plasma induce the breakdown of gases in surrounding atmospheres. To identify the environmental gas breakdown, collected emission spectra were compared with both the molecular and atomic emission spectra of the surrounding gas elements. Molecular and atomic spectral data of nitrogen, oxygen, argon and helium [95, 96] are used for the identification. The results were also compared with other LIBS studies for ambient air breakdown [106, 107].

Figure 61 shows the identification of molecular breakdown of nitrogen and oxygen gases. In the all gas processing conditions, no prominent feature was identified in both the molecular nitrogen and the molecular oxygen emission spectra. The lack of molecular emission spectra indicates that the relaxation of excited nitrogen and oxygen occurred by transitions of atomic energy levels, rather than transitions of neutral molecules [107].



Figure 61. Identification of molecular environmental-gas breakdown from the LIBS on CVD diamond film

The laser-induced breakdown of ambient air produces free electrons and ionized nitrogen and oxygen atoms. The recombination of the free electrons and the ionized atoms generates atomic line spectra as the excited electrons relax to the ground states. Then, the atomic nitrogen and oxygen combine to form molecular nitrogen and oxygen. However, the atomic recombination does not have sufficient internal energy to generate molecular line spectra in the observed wavelength range [107]. In LIBS in this study, the atomic emission route of nitrogen and oxygen is supported by the absence of molecular emission spectra and the presence of atomic emission spectra.

Figure 62 shows the identification of atomic gas breakdown for the nitrogen, oxygen, helium and argon. In the ambient air, relatively weak signals of OI 777.19 \sim 777.54 nm and NI 404.13 \sim 404.35 nm are identified. In the argon gas steaming condition, the well-known intense argon neutral emission spectra are shown in the range between ArI 696.53 nm \sim ArI 811.54 nm. The atomic nitrogen spectra are also shown at NI 567.60 nm \sim 568.62 nm, NII 592.78 nm \sim 595.24 nm and NII 642.06 nm \sim 643.77 nm. In the helium gas steaming condition, no indication of helium gas breakdown was observed. The identified atomic spectra of nitrogen and oxygen are significantly reduced in the helium gas-streaming condition. Only traces of the weak atomic oxygen spectra (OI 777.19 \sim 777.54 nm) and the weak atomic nitrogen spectra (567.60 \sim 643.77 nm) were found near the continuum background.

By combining the atomic and molecular spectra, Figure 63 and Figure 64 list the all identified emission spectra found in LIBS on the CVD diamond film.



Figure 62. Identification of atomic environmental-gas breakdown from the LIBS on CVD diamond film



Figure 63. Identified line emission spectra by LIBS on the CVD diamond film in the wavelength region 350 nm ~ 600 nm.



Figure 64. Identified line emission spectra by LIBS on the CVD diamond film in the wavelength region 550 nm ~ 825 nm.
5.1.4. Influence of laser irradiances on emission spectra

To observe the influence of laser irradiances on the emission spectra, the diamond film was subjected to various laser irradiances from 2.4×10^8 W/cm² to 8.4×10^8 W/cm², with an increment of 1.2×10^8 W/cm². The gas processing environments were ambient air, helium gas-stream and argon gas-stream. The gas flow rate was constant at 5×10^4 m³/sec for the helium and argon gases. Carbon molecular emissions are observed in lower intensities than those for the carbon atomic and ionic emissions. The molecular carbon bands have been well observed in the laser irradiance over 10^6 W/cm² [68, 69, 74, 93, 100, 108]. The carbon atomic and ionic emissions require that the laser irradiance reach 10^8 W/cm² [69, 100]. Due to the high laser irradiance range (2.4×10^8 W/cm² to 8.4×10^8 W/cm²) of this study, the carbon molecular emission spectra were observed in all laser irradiation levels. The carbon atomic and ionic emission spectra were weak at the low laser irradiances near 2.4×10^8 W/cm².

Figure 65 shows the intensities of plasma emission spectra in the ambient air. As the laser irradiance increased, both the background and the line spectra were increased. In the ambient air, the strong CN Violet bands are dominant in all irradiance levels. The C_2 Swan bands appear at the lowest laser irradiances, and the intensity of the bands are increased with the laser irradiance. In contrast to the molecular emissions, the atomic emission spectra were not prominent at the low laser irradiances.



Figure 65. Laser-induced plasma emission spectra on the diamond film in ambient air as a function of the laser irradiance.

As indicated by CII 657.81 nm and OI 777.19 ~ 777.54 nm, the atomic spectral intensities at 2.4×10^8 W/cm² are hardly recognized in the continuum background. As the laser irradiance increased, the atomic spectra were becoming prominent. This tendency was also observed in CII 657.81 nm in argon gas-streaming in Figure 66. The influence of the laser irradiance on CN Violet bands and C₂ Swan bands in argon gas-streaming was analogous to that on the molecular bands in the ambient air. The breakdown of argon gas was clearly observed by the intense singly-ionized argon (ArI) peaks in all laser irradiance levels. Even though helium gas-streaming in Figure 67 exhibited relatively low molecular emission spectra, the dependence of the spectral intensity on the laser irradiance on was similar to the other gas processing conditions. The helium gasstreaming exhibited the most intensive carbon ion emission spectra among the gas processing conditions. The CII 657.81 nm in Figure 67 showed relatively high emission intensities even at the lowest laser irradiance. The singly ionized oxygen, OI 777.19 \sim 777.54 nm, in helium gas processing condition showed the evolution of emission intensity similar to that of the ambient air.

The relationship between spectral intensity and laser irradiation are important to analyze properties of the laser-induced plasma. From Figure 68 to Figure 70, dependence of emission intensities on laser irradiance is shown among the gas processing conditions. The emission spectra and continuum background, as well as the ratio between those, are plotted as a function of the laser irradiances. A representative spectrum was chosen for each of the major molecular and atomic emission systems.



Figure 66. Laser-induced plasma emission spectra on the diamond film in argon gasstreaming as a function of the laser irradiance.



Figure 67. Laser-induced plasma emission spectra on the diamond film in helium gasstreaming as a function of the laser irradiance.



Figure 68. In the ambient air, the intensities of the emission spectra and the continuum background are plotted as a function of the laser irradiance, a) C₂ Swan band, b) CN Violet band, and c) CII. Corresponding ratios of the emission spectra to the background are shown in, a-1) C₂ Swan band, b-1) CN Violet band, and c-1) CII. The guide lines are arbitrarily drawn to show trends of the data.



Figure 69. In the helium gas-streaming, the intensities of the emission spectra and the continuum background are plotted as a function of the laser irradiance, a) C₂ Swan band, b) CN Violet band, and c) CII. Corresponding ratios of the emission spectra to the background are shown in, a-1) C₂ Swan band, b-1) CN Violet band, and c-1) CII. The guide lines are arbitrarily drawn to show trends of the data.



Figure 70. In the argon gas-streaming, the intensities of the emission spectra and the continuum background are plotted as a function of the laser irradiance, a) C₂ Swan band, b) CN Violet band, and c) CII. Corresponding ratios of the emission spectra to the background are shown in, a-1) C₂ Swan band, b-1) CN Violet band, and c-1) CII. The guide lines are arbitrarily drawn to show trends of the data.

The C_2 Swan bands at 516.52 nm, CN Violet bands at 388.34 nm and carbon atomic emission at CII 657.81 nm were selected for the comparison among the gas processing conditions. For the continuum backgrounds, the nearest continuum level of the each representative spectrum was used.

In Figure 68, the emission intensities in ambient air are shown as a function of laser irradiance. The guide lines are arbitrarily drawn to show trends in the data. In Figure 68a~c, all of the emission spectra and continuum background exhibit increases in their intensities as the laser irradiance increases. The largest gap between emission spectrum and continuum background in Figure 68b illustrates the most intensive emission of CN Violet bands in the ambient air. In the lowest laser irradiance, the singly ionized carbon spectrum at 657.81 nm in Figure 68c shows the smallest spectral intensity difference between the spectrum and the continuum background. The spectral intensity of CII 657.81 nm drastically increased with an increase in the laser irradiance, which substantiates the active ionization of carbon atoms in higher laser irradiances. In the C_2 Swan bands (Figure 68a-1) and CN Violet bands (Figure 68b-1), the ratios of the emission spectrum to the continuum background were decreased as the laser irradiance increased. This indicates the substantial increase in continuum background emission in high laser irradiance, as compared to the molecular emission spectra. In contrast, the ratio of CII 657.81 nm to continuum background was increased with an increase in the laser irradiance. The increasing ratio indicates the active ionization of carbon atoms in higher energy laser irradiance region.

In Figure 69, the emission intensities as a function of laser irradiance are shown for the helium gas-streaming condition. Similar trends were observed for all of the emission spectra and continuum background, and they exhibit increases in their intensities as the laser irradiance increases. The spectral intensity of CII 657.81 nm also showed drastic increases with an increase in laser irradiance. Consistent with the observation in ambient air, the molecular emission bands, C_2 Swan (Figure 69a-1) and CN Violet (Figure 69b-1), exhibited the decrease in ratios of the emission spectrum to the continuum background. The increase in the ratio of CII 657.81 nm in Figure 69c-1 was observed as well.

The relationship for the argon gas-streaming condition is shown in Figure 70 that the trends were analogues to the observations in ambient air and helium gas-streaming. In Figure 70a~c, the increase in laser irradiance resulted in an increase in emission spectra for both the line spectra and continuum backgrounds. The C_2 Swan bands in Figure 70a exhibited the most intense spectral emission, as compared to the their continuum background. The smallest difference of the spectral intensity was found between the singly ionized carbon emission (Figure 70c) and its continuum background. The behavior of the spectrum to the background ratios was consistent that the descending trend was found in the molecular emission spectra (Figure 70a-1 and b-1). The ascending trend of the ratio was also found in the atomic carbon emission (Figure 70c-1).

Regardless of the gas processing environments, the measured intensities of the emission spectra and continuum backgrounds behaved as an exponential function of laser irradiance. The behavior of the spectral intensity, which is proportional to the concentration of the molecular and atomic species, can be modeled by the exponential function:

$$I(r) = I_o \cdot e^{a\left(\frac{r-r_o}{r}\right)}$$
 Equation 20

where I(r) is a spectral intensity (arbitrary unit) at laser irradiance r, I_o is spectral intensity at the detection threshold, a is an irradiance coefficient, r is a laser irradiance (W/cm²), and r_o is a laser irradiance at the detection threshold. The irradiance coefficient a is an empirical constant, which depends on energy levels of the spectrum and environmental factors of the laser irradiation. The irradiance coefficient can be obtained by boundary conditions of the measured intensities. Figure 71 shows the agreements between the measured emission intensities and the proposed relationship in Equation 20. The emission intensities of C₂ Swan band at 516.52 nm, CN Violet band at 388.34 nm, and CII 567.81 nm were subjected to the equation, which modeled exponential relationship between the emission intensities in the scattered points showed good agreement to the modeled exponential functions in the curved lines. The irradiance coefficient a, displayed in the Figure 71, were obtained from Equation 20 by inserting lower and upper boundary values of the spectral intensity and the laser irradiance.

5.1.5. Excitation temperature of the laser-induced plasma

The temperature of the laser-induced plasma is one of the most important applications of quantitative LIBS. Measuring temperature of an excitation source helps to understand the dissociation, atomization, ionization and excitation processes [68-70, 74, 78, 82, 83, 85, 86, 89-91, 97, 100, 108-111]. The excitation temperature of the plasma can be deduced by an assumption that the plasma is in local thermodynamic equilibrium (LTE).



Figure 71. Modeling of the emission intensity of the CVD diamond as a function of the laser irradiance for the various gas processing conditions; a) C₂ Swan band at 516.52 nm, b) CN Violet band at 388.34 nm, and c) CII 567.81 nm. The displayed values of irradiance coefficient a were obtained by lower and upper boundary values of the emission intensities and laser irradiances.

The plasma in LTE follows the Boltzmann distribution of electronic states of atoms and molecules for a given temperature in a localized area. The excitation temperature is calculated by emission intensity ratios from different upper energy levels of an element in the same electronic state.

Using the vibrational quantum number v, the transition from an upper molecular vibrational level v' to an lower molecular vibrational level v'' is denoted by (v', v''). The intensity of spectral emission, resulted from the transition (v', v''), can be related to the initial state molecular population [108]:

$$I_{\nu'\nu'} = KN_{\nu}A_{\nu'\nu'}\left(\frac{hc}{\lambda}\right)$$
 Equation 21

where $I_{vv'}$ is the intensity of a spectral emission from the transition of molecular vibration level v'to v", K is proportionality constant (cm³·sec/J) related to the sensitivity of the acquisition, N_v is the number population (cm⁻³), $A_{vv'}$ is Einstein transition probability of spontaneous emission (sec⁻¹), h is the Plank constant (6.63×10⁻³⁴ J·sec), c is the speed of spectral emission (m/sec), and λ is wavelength (nm) of the spectral emission. According the wave mechanics in radiation, the Einstein transition probability is related to the electron transition moment [108]:

$$A_{\nu'\nu'} = \frac{64\pi^4}{3h\lambda^3} (R^{\nu'\nu'})^2 \qquad \qquad \text{Equation 22}$$

where $R^{\nu\nu}$ is the transition moment. Then the intensity of spectral emission can be written as:

$$I_{vv^*} = \left[\frac{64\pi^4 c K \left(R^{vv^*}\right)^2}{3}\right] \left(\frac{N_v}{\lambda^4}\right)$$
 Equation 23

The terms, c, K and $R^{\nu\nu}$ are not variables in the equation. Substitute the constant terms for C_1 and rewrite the equation for the relationship among $I_{\nu\nu}$, N_{ν} , and λ :

$$I_{\nu\nu^*} = C_1 \left(\frac{N_{\nu}}{\lambda^4} \right)$$
 Equation 24

When the plasma is in LTE, the number population N_{ν} is given by the Maxwell-Boltzmann equation [85, 86, 108]:

$$N_v = N_o \cdot e^{\frac{E_v}{kT}}$$
 Equation 25

where N_o is the total number population (cm⁻³), E_v is energy state at the molecular vibrational level v, k is the Boltzmann constant (1.38×10⁻²³ J/K), and T is the excitation temperature (K). The vibrational energy E_v can be obtained by the relationship to the term value G_v [108]:

$$G_v = \frac{E_v}{hc} = \omega(v + \frac{1}{2})$$
 Equation 26

where ω is the measured vibrational frequency in cm⁻¹, and the ν is the vibrational quantum number. Combining Equation 24, Equation 25 and Equation 26, rearranging and taking natural logarithm give the equation:

$$\ln(\lambda^4 I_{v'v'}) = \ln(C_1 N_o) - \left(\frac{hc}{kT}\right) G_v \qquad \text{Equation 27}$$

Finally, the equation for the excitation temperature can be expressed by considering various molecular vibration energy levels, and substituting the constant term for C [69, 70, 74, 108]:

$$\ln \sum \left(\lambda^4 I_{v'v'}\right) = C - \left(\frac{hc}{kT}\right) G(v) \qquad \text{Equation 28}$$

In Equation 27, a plot of $\ln(\lambda^4 I_{\nu\nu})$ in various vibrational levels as a function of $G(\nu)$, at a constant temperature T, yields a linear relation with a slope equal to -(hc/kT) and a interception C. The excitation temperature T can be calculated from the slope of the plot.

For the spectroscopic measurements the temperature of the molecular excitation, distinctive emission peaks in various vibrational energy levels are required. In this study, the C_2 Swan bands appeared prominent in all of the gas processing conditions and all of the irradiance levels. The emission spectra of the C_2 Swan bands in various vibrational transition levels, 516.52 nm (0,0), 512.93 nm (1,1) and 509.77 nm (2,2) were chosen to deduce the excitation temperature. The locations of the emission spectra are indicated in Figure 72.

For the plot of $\ln(\lambda^4 I_{vv})$ as a function of G(v) in Equation 28, the emission intensities I_{vv} were measured from the Figure 65, Figure 66 and Figure 67. G(v) is obtained by Equation 26 with tabulated ω [108]. Figure 73 shows the plots for $\ln(\lambda^4 I_{vv})$ as a function of G(v) in various laser irradiances in the gas processing conditions. The linearity of the data was assumed, and the slopes of the linear lines were calculated. The calculated values of the slopes were displayed in Figure 73.



Figure 72. Emission spectra of the C_2 Swan bands in various vibrational transition levels used for the temperature measurements.

Figure 74 shows the excitation temperature of the C_2 Swan bands in various gas processing conditions as a function of laser irradiance. The deviation ranges displayed by the error bars resulted from the regression range of the linear fit for the data in Figure 73. The deviation range observed in this study was 6% ~ 25%. Typical accuracy ranges were reported about 80% ~ 95% in spectroscopic temperature measurements [74]. The uncertainty of this temperature measurement depends on the existence of the assumed LTE, the accuracy of the instrumentation and the error range of spectroscopic constants of the molecular emission lines.



Figure 73. $\ln(\lambda^4 I_{\nu\nu\nu})$ in various vibrational levels as a function of $G(\nu)$ in various laser irradiances in the gas processing conditions, a) ambient air, b) helium gas processing, and c) argon gas processing.



Figure 74. Excitation temperature of the C_2 Swan bands in various gas processing conditions as a function of laser irradiance.

The temperatures measured in Figure 74 are deduced from time-integrated intensities, which provide average temperature values for the molecular excitation. In all gas processing conditions, the excitation temperature was increased as the laser irradiance increased. The rate of increase in temperature appeared to be approximately constant for all of the gas processing conditions. The plasma in ambient air showed the highest excitation temperatures in the given irradiance range. The excitation temperature reached to 3.9×10^4 (K) at the laser irradiance 8.4×10^8 W/cm² in the ambient air. In contrast, the excitation temperature in the argon gas-streaming showed the lowest profile in the

irradiance range. The temperatures observed in the argon gas-streaming were about 45%, in average, lower than those in the ambient air. In the helium gas-streaming, the excitation temperatures were about 25% lower than those in the ambient air.

5.1.6. Electron density of the laser-induced plasma

In plasma, the emitting atoms or ions are under the influence of electric fields, which are produced by relatively rapidly moving electrons and slowly moving atoms and ions. The pressure broadening of a line spectrum is caused by perturbations of the electric field by collision of the charged particles that contains a permanent dipole moment [85, 86]. Because the electric filed is involved, it is called the Stark broadening. By studying the well-known hydrogen lines, the Stark broadening was found out to be proportional to the density of the charged species [85]. From the linear Stark effect, the broadening of a line spectrum is proportional to the two-thirds power of the ion density, which is equal to the electron density. The relation assumes that only the first ionization is important and the second ionization equilibrium is not important. The proportionality between the line broadening and electron density is expressed by:

$$n_{c} = C(n_{c}, T) \Delta \lambda^{3/2}$$
 Equation 29

where n_e is the electron density (cm⁻³), $C(n_e,T)$ is a coefficient that is only a weak function of electron density and temperature, and $\Delta\lambda$ is full Stark broadening width. The Stark broadening was compensated by considering two extreme broadening mechanisms, quasi-static approximation and impact approximation [85, 86]. The quasi-static approximation is valid when the particles move relatively slowly, so that the perturbation is practically constant over the time. The perturbation is described by the order of the inverse of the line broadening width. In contrast, the impact approximation assumes unperturbation of the emitting systems, and describes the line broadening by the impact theory of quantum mechanics [86]. According to the approximations, the compensations was made on the coefficient $C(n_e,T)$ with parameters of the electron impact and ionbroadening. A practical equation for the spectroscopic measurement of the electron density is suggested by [68, 85, 86, 90]:

$$\Delta \lambda = 2\omega \left(\frac{n_e}{10^{16}} \left[1 + 4.75\alpha \left(\frac{n_e}{10^{16}}\right)^{\frac{1}{4}} \left(1 - 0.068 \left(\frac{n_e}{T}\right)^{\frac{1}{6}} \right) \right]$$
 Equation 30

where ω is electron-impact half width (nm), n_e electron number density (cm⁻³), α is ionbroadening parameter, and T is the temperature (K). The parameter α is obtained by correlation between the peak broadening and the electric field strength of singly charged ions [85].

In this study, the carbon neutral spectral emission line (CI) at 477.18 nm (see Figure 63 for the peak identification) was measured for the Stark broadening width $\Delta\lambda$ using full width half maximum (FWHM) of the peak. The FWHM of CI 477.18 nm was measured in all gas processing conditions for comparison. The Stark broadening were measured in higher irradiance levels of 6.0, 7.2 and 8.4×10^8 W/cm², which exhibited distinctive peaks at CI 477.18 nm. The measured $\Delta\lambda$ values are in Table 11.

	$6.0 \times 10^8 \text{ W/cm}^2$	$7.2 \times 10^8 \text{ W/cm}^2$	$8.4 \times 10^8 \text{ W/cm}^2$
ambient air	3.94 nm	4.51 nm	4.84 nm
helium gas-streaming	2.50 nm	2.68 nm	2.91 nm
argon gas-streaming	2.11 nm	2.51 nm	2.79 nm

Table 11. Measured FWHM values for the $\Delta\lambda$ (nm) in various gas processing conditions and laser irradiances (W/cm²).

The measured $\Delta\lambda$ are inserted in Equation 30 for the electron density calculations. The values of the electron-impact half width ω and the ion-broadening parameter α are well tabulated in references [85, 86] for the carbon atomic emission spectra. The ω and α values for the CI 477.81 nm spectrum were 0.0157 nm and 0.043, respectively [86]. Since Equation 30 is the weak function of the temperature, a rough estimation of the temperature can be assumed for the calculation [68, 85, 86, 112]. This assumption was verified in this study that the variation in temperature rage of 10⁵ resulted in less than 0.1% of the variation in the calculated density. The estimated value of 2000 K was used for the calculation [68].

Figure 75 shows the calculated electron densities in various gas processing conditions as a function of the laser irradiance. The electron densities in Figure 75 are calculated from time-integrated intensity of the emission spectrum, which provide average electron density values of the laser-induced plasma. In the given range of the laser irradiance, all gas processing conditions exhibited an increase in the electron densities as the laser irradiance increased. The densest population of electrons was found in the density profile of the ambient air.



Figure 75. Electron density in various gas processing conditions as a function of the laser irradiance.

The electron density in ambient air reached to 1.6×10^{18} cm⁻³ at the laser irradiance 8.4×10^8 W/cm². The argon gas-streaming showed the lowest density profile among the processing conditions. The helium gas-streaming showed slightly higher density profile than that of argon gas-streaming, but significant differences were also found as compared to the density profile in the ambient air.

There are a few sources that cause uncertainty of the calculated electron densities [85, 86]. The instrumentation, which requires precise measurement of FWHM of the line spectrum, is one source of errors. In the case of weak or very broad lines, it is difficult to not only determine the underlying continuum background but also differentiate the contributions from other line spectra. The calculated Stark broadening parameters also

contain up to 10% of uncertainties. Errors can be caused when substantial amount of self-absorption occurs and when electron density changes in the acquired spectra. The Doppler broadening, which is caused by kinetic temperature of emitted atoms and ions, can be the most important competing broadening mechanism. However, the Doppler broadening is negligible in LIBS, which involves dense laser-induced plasma with neutral or singly ionized emission spectra [68, 74, 84-86, 90]. All these possible sources of uncertainty reduce the reliability of the absolute value of the calculated electron densities. However, the relative value among the calculated electron densities, in which the emission spectra are acquired in the same instrumentation, have reasonably high reliability from the proved nature of the Stark broadening. The reliability of the relative value gives strong credibility on the comparison of measured electron densities among the gas processing conditions in this study.

5.1.7. Physical and chemical interpretation of the emission spectra

In this LIBS study on the CVD diamond film, the most active carbon emission systems were C₂ Swan bands, CN Violet bands and atomic CI and CII spectra. The atomic CI and CII spectra appeared distinctive in higher irradiance range (> $\sim 4 \times 10^8$ W/cm²). The breakdown of environmental gases was also observed by atomic emission spectra of nitrogen, oxygen and argon. The molecular emission spectra, C₂ Swan bands and CN Violet bands, were prominent throughout the entire irradiance range (2.4×10⁸ W/cm² to 8.4×10⁸ W/cm²) in this study. The physical and chemical interpretation of the molecular emission bands leads this study to the better understanding on the laser-induced plasmas on the CVD diamond film.

5.1.7-a. C: Swan bands

The C_2 Swan bands appeared in emission spectra of all gas processing conditions. The C_2 Swan bands resulted from relaxation of excited C_2 molecules. The argon gasstreaming showed the most intensive emission spectra of the Swan bands, while the ambient air showed the lowest intensities. High electron density of laser-induced plasma, with increased population of charged particles, stimulates the emission for the Swan bands. The origins of the Swan bands have been suggested from other spectroscopic investigations on carbon species [68, 69, 89, 100].

When the laser-induced plasma expands to the ambient after the termination of the laser pulse, the high-energy electrons in the plasma start to lose their energy. Then, the excited states of molecules, atoms and ions are created by heavy-body collisions, ionelectron/ion-ion recombination, and electron-molecule dissociative recombination [113]. Heavy-body collisions of metastable atoms and metastable molecules, called Penning collision, is considered as a weak but possible mechanism for producing the Swan bands through excited C_2 molecules. The presence of Penning collision tends to increase the continuum background [100]. The ratios of the emission spectra to the continuum background were observed in Figure 68, Figure 69 and Figure 70 for the Swan bands. The consistent decrease in the ratios as a function of the laser irradiance indicates the relative increase in the continuum background to the emission spectra. The increase in the continuum background is the plausible indication of the presence the Penning collision. However, the contribution of Penning collision to the excitation of C_2 molecules are negligibly small as compared to other strong mechanisms [100]. One of the electron-ion recombination processes is a two-body collision between an electron and a C_2 cation:

$$e^- + C_2^+ \rightarrow C_2^+$$
 Equation 31

where the '*' indicates the excited stage. This appears to be the most direct and plausible mechanism to create excited C_2 molecule, but other investigations [100, 114] have shown that it is unlikely due to the rapid energy loss of colliding electrons. The electrons in expanding plasma lose their energy rapidly into ambient, which reduces their energy far less than ~ 3 eV for the recombination [114]. The other electron-ion mechanism is a three-body collision among an electron, a C_2 cation and a neutral inert gas atom. In this study, helium and argon were used for dynamic streaming gases, which result in the three-body processes:

$$e^- + C_2^+ + He \rightarrow C_2^* + He$$
 Equation 32
 $e^- + C_2^+ + Ar \rightarrow C_2^* + Ar$ Equation 33

The third body, the neutral inert gas atom, assists the process by transporting its excessive energy to the colliding electron. The electron gains energy from the third-body collision partner to form the excited C_2 molecule [97, 100]. The energy to create an excited argon atom is much lower than that to create an excited helium atom. For example, the first ionization energy of argon is 15.76 eV and that for helium is 24.59 eV [95]. Hence, the three-body process with argon is expected to be more likely than that with helium. This speculation is supported by the LIBS in this study in which the C_2 Swan bands were much more intensive in argon gas-streaming than in helium gas-streaming (see Figure 59). Accordingly, the ambient air without the inert collision partner showed the lowest intensity of the Swan bands. The strong plausibility of Equation 33 is furthermore supported by the abundance of the intense argon neutral atomic spectra in this study (see Figure 64). The abundance of excited argon neutral atoms leads to another plausible mechanism by charge exchange:

$$C_2^+ + Ar^* \rightarrow C_2^* + Ar^+$$
 Equation 34

This charge exchange between an excited argon atom and a carbon cation strengthens the intense Swan bands in the argon gas-streaming in this study. Similar to the case discussed in the three-body process, the high ionization potential of helium makes the generation of Swan bands via the charge exchange unlikely in the helium gas processing condition.

The C_2 Swan bands can be produced by ion-ion recombination in which carbon cation and anion are recombined to form excited C_2 molecule:

$$C^+ + C^- \rightarrow C_2^+$$
 Equation 35

The atomic cation and anion recombination is regarded as a plausible mechanism for laser irradiance over 10^8 W/cm² due to the increase in population of ionic particles at the high laser irradiance regime [114]. In this study, the plasma was induced by the laser irradiance levels over 10^8 W/cm². The atomic CI and CII spectra appeared distinctive in irradiance range over ~ 4×10^8 W/cm² (see Figure 63 through Figure 67). This is a good indication of increased population of carbon ionic reactants in the laser-induced plasma. However, the population of the atomic anions in the laser-induced plasma is expected to be orders of magnitude smaller than that of the atomic cations and electrons [7, 115]. Accordingly, the probability of the recombination between the carbon cations and anions

is much more smaller than that of the recombination between the carbon cations and electrons. Thus, the carbon cation and anion recombination is a weak but plausible mechanism for the production of the Swan bands in high laser irradiance regime.

The most plausible mechanisms for spectral emission of the Swan bands is the electron recombination with C_n cations (n > 2) and metastable C_n molecules (n > 2), which results in dissociation of excited C_2 molecules:

$$e^- + C_n^+ \rightarrow C_{n-2} + C_2^*$$
 Equation 36
 $e^- + C_n^* \rightarrow C_{n-2}^- + C_2^*$ Equation 37

This mechanism is called dissociative recombination where the excited C_2 molecules are relaxed to the ground state emitting the C_2 Swan bands. As *n* increases in the C_n clusters, the conditions for dissociative recombination become more likely. This is due to the increase in internal degrees of freedom, in which electrons can be coupled to dissociate the excited C_2 molecules. Several investigations on laser-induced plasmas [68, 89, 98, 99, 111] have shown the abundance of the carbon clusters, which are formed by both the multiphoton fragmentation upon the laser irradiation; and the nucleation from carbon vapor consisting of carbon atoms and small carbon molecules. The carbon clusters in laser-induced plasma showed copious distribution of small clusters (n < 30) and larger clusters, as large as n > 400. These carbon clusters increase the number of pathway by which the dissociative recombination in Equation 36 and Equation 37 can take place. The statistically high chances of the reactions make the dissociative recombination process the most plausible. Early investigations on carbon emission spectra [100, 113, 114] found evidences for the presence of two distinctive velocity distributions of the bulk emissions. The significant attribution of dissociative recombination was confirmed in the recent investigation [98] by measuring the time-of-flight emission spectra on a graphite target. In the investigation, the faster velocity components were explained by emissions generated from the recombination processes, and the slower components were attributed to dissociative recombination of the carbon clusters resulting in the generation of C_2 molecule.

5.1.7-b. CN Violet bands

The CN Violet bands can be produced by ion-ion combination in which carbon and nitrogen ions are collided to form excited CN diatomic molecule:

$$C^+ + N^- \rightarrow CN^*$$
Equation 38 $C^- + N^+ \rightarrow CN^*$ Equation 39

The nitrogen cations are assumed to be abundant from the observation of the nitrogen gas breakdown in all laser irradiance levels in this study. Increased population of the carbon atomic cations are also observed in laser irradiance over ~ 4×10^8 W/cm². However, the population of the atomic anions is expected to be orders of magnitude smaller than that of the atomic cations and electrons [7, 115]. Hence, the probability of the recombination between cations and electrons is much more higher than that of the combination between cations and anions. The relatively small population of anion reactants makes the ion-ion combination a weak mechanism for the CN Violet bands.

According to the speculations discussed in the dissociative recombination for the C_2 Swan bands, the abundance of the carbon clusters in the laser-induced plasma supports a plausible pathway for the CN Violet bands:

$$C_{n}^{*} + N^{*} \rightarrow C_{n-1} + CN^{*}$$
Equation 40
$$C_{n}^{*} + N^{*} \rightarrow C_{n-1}^{*} + CN^{*}$$
Equation 41

The proposed reactions involve the generation of excited gaseous CN by dissociative combination between a carbon cluster (n > 2) and an excited neutral nitrogen atom. The neutral nitrogen atom is activated in the laser-induced plasma, and collides to the metastable carbon cluster and the cation carbon cluster, as shown in Equation 40 and Equation 41, respectively. In this study, the dissociative combination is also supported by observation of the breakdown of nitrogen gas (see Figure 62 ~ Figure 64), which generates sufficient amount of reactive nitrogen atoms. The CN Violet bands by the dissociative combination are the most intensive spectral emissions in the ambient air in this study (see Figure 63 ~ Figure 65). Thus, it can be assumed that the abundance of nitrogen in ambient air transformed the laser-induced carbon clusters into gaseous CN molecules. In this speculation, substantial amount of laser-ablated carbon species has to be vaporized by the reaction in Equation 40 and Equation 41. The observation on ablation debris supports the significant vaporization of carbon cluster in the ambient air.

Figure 76 shows the ablation debris deposited around the irradiation spots among the gas processing conditions. In Figure 76a, the laser irradiation in ambient air resulted in a significant decrease in ablation debris, as compared to Figure 76b and c in other gas processing conditions. The magnified views of the near spot area in Figure 76a-1, b-1 and c-1 also prove that the ambient air in Figure 76a-1 shows significantly decreased debris deposition, as compared to the helium gas-streaming in Figure 76b-1 and the argon gas streaming in Figure 76c-1.



Figure 76. Comparison of ablation debris around the irradiation spots among the gas processing conditions; (a) and (a-1) ambient air, (b) and (b-1) helium gasstreaming, and (c) and (c-1) argon gas-streaming.

Thus, it is conclusive that the laser-irradiation in ambient air, in which the CN Violet bands are the major emission spectra, resulted in significant formation of gaseous carbonitride molecules. Other gas processing conditions, in which the major emission spectra was the C_2 Swan bands, showed larger amounts of debris deposition. The argon gas steaming in Figure 76c shows the largest amount of deposited debris due to the breakdown of the argon gas. As discussed in the mechanisms for the Swan bands, the breakdown of argon gas results in the abundance of electrons, and excited argon neutrals and ions, which promoted the formation of C_2 molecules by the additional mechanisms, such as the electron-ion interaction (Equation 33) and the charge exchange (Equation 34). As compared to the argon gas-streaming, relatively small amount of ablation debris were found in the helium gas-streaming, in which the plausible mechanism was only the dissociative recombination in Equation 36 and Equation 37.

5.2. Images of Laser-Induced Plasma

5.2.1. Interaction of laser-induced plasma

An incident pulsed laser beam interacts with a target material in photothermal and photochemical processes [23, 38, 78]. In the photothermal process, the absorption of photons leads to the excitation of electrons, which consequently transfers the energy in the form of heat to the lattice. Melting and evaporation occur, and the high-temperature plasma is induced from the energy transfer. In photochemical process, the absorbed photon energy is dissipated through breaking of chemical bonds, which results in instantaneous evaporation, called the ablation.

Figure 77 shows the schematic diagram for the interaction of the laser-induced plasma to its surrounding. The high-temperature plasma interacts with the surrounding in two ways. Firstly, the expansion of the high-pressure plasma drives shock waves into the surrounding, and secondly, energy is transferred to the surrounding by a combination of thermal conduction, radiative transfer, and heating by the shock waves [23, 27, 78]. Even though the laser-material interaction is limited to nanoseconds to femtoseconds ranges for most of the pulsed lasers, the plasma extends far longer than the laser pulse duration [27, 71, 116]. The duration of the plasma has been observed in tens of microseconds.



Figure 77. Interaction of laser-induced plasma to the surrounding [23, 27, 78].

The evolution of the plasma depends on laser irradiance, composition of a target martial, laser wavelength, and ambient gas composition and pressure.

The expanding plasma can transfer significant amount of energy to the target surface by thermal conduction, and radiation. The plasma-material interaction gives rise to changes, such as surface phase transformation, material ejection and re-deposition, and spoiled interfaces. Observation of the plasma, by image capturing, is valuable to characterize details of the expansion of the plasma.

5.2.2. Image capturing of laser-induced plasma

The experimental setup for the image capturing is shown in Figure 78. The plasma was induced on a CVD diamond film (ST235), which has an average thickness of 110 μ m and average grain size of 50 μ m. The laser in the setup is the KrF excimer laser (Lambda Physik[®], model COMPex 301) with a wavelength of 248 nm, a rectangular pulsed beam of 1.3×3.0 cm² in TEM₀₀ mode, a maximum pulse energy of 1.5 J and a maximum repetition rate of 10 Hz. The focused spot size used for the image capturing is 650 μ m in diameter. The spot size was produced by the imaging optics, which includes an automatic aperture unit, and a set of planar convex lenses (focal lengths 295 mm and 50 mm). Three gas nozzles are installed around the objective lens to deliver regulated dynamic gas-stream over the irradiation spot. The nozzles are positioned about 3 mm from the irradiated spot, and 30° degrees to the film surface.

A charge coupled device (CCD) camera was used to capture the time integrated images of the laser-induced plasma. The CCD camera used for the capturing was Javelin[®], model Chromachip II, equipped with a convex objective lens in 27 mm focal length. The CCD camera was positioned at 20° angle to the target surface. The image capturing was synchronized with the pulsed laser irradiation at 10 Hz repetition rate, and 7.5×10^8 W/cm² laser irradiance. The captured signals are transferred to the video image board, Matrox[®] Marvel G200, for digital image processing. The CCD camera and the video board were set to 100 µs acquisition time frame for the synchronization to the laser pulse repetition rate of 10 Hz.



Figure 78. Schematic diagram for the time-integrated image capturing of laser-induced plasma on the CVD diamond film.

Optical filters, band pass 400 nm (BP400), and long pass 525 nm (LP525), were placed to screen the intense reflection from the laser beam, and to illuminate the extent of the expanding plasma. The wavelength pass ranges of the optical filters are shown in Figure 79.



Figure 79. Plots showing wavelength pass ranges for the optical filters; a) band pass filter BP400, and b) long pass filter LP525.
5.2.3. Time-integrated images of laser-induced plasma

5.2.3-a. Laser induced plasma on CVD diamond

Figure 80 shows an example of the synchronized capturing of the time-integrated images of plasma. The series of images were taken from the argon gas-streaming without the optical filter. Each image was obtained by 100 μ s time-integrated acquisition, from a single pulse of the laser irradiation at 25 ns. Among the series of acquired images, representative sets of the plasma images are shown in Figure 81 for the ambient air, Figure 82 for the helium gas steaming, and Figure 83 for the argon gas-streaming. From the time-integrated plasma images, the extent of the laser-induced plasma is compared.

Figure 81 shows the plasma images captured in the ambient air. Unfiltered image in Figure 81a shows not only the image of the laser-induced plasma, but also the intense reflection of the incident excimer laser. The intense reflection of the laser beam is filtered by a BP400 filter in Figure 81b. The brightest region at the center of the irradiation spot indicates the most intense irradiation near the wavelength of 400 nm. The extent of expanding plasma over wavelength 525 nm is shown in Figure 81c, filtered by the LP525 filter. The lowest longitudinal expansion of the plasma was observed in the ambient air. In contrast, the lateral expansion of the plasma is relatively strong. The lateral expansion is prominent in Figure 81c, in which the ejection of large particles (indicated by the arrow) was frequently observed.



Figure 80. Example of the synchronized capturing (100 μ s time frame acquisition for the 10 Hz irradiation) of the time-integrated plasma images. Each image is captured by 100 μ s integrated-acquisition from a single pulse of the laser irradiation.



Figure 81. Time-integrated image of laser-induced plasma on the CVD diamond film in ambient air; a) unfiltered image, b) image captured with BP400 filter, and c) image captured with LP525 filter, the arrow indicates the ejection of a large particle.

The images of the plasma for the helium gas processing are shown Figure 82. An unfiltered image, in Figure 82a, shows a more spherical-type of expansion than that for the other gas processing conditions. In Figure 82b, the lateral expansion is significantly reduced as compared to the ambient air. In contrast, the longitudinal expansion is more prominent than that in the ambient air. Figure 82c, with the LP525 filter, consistently shows the prominent expansion in the direction normal to the target surface. At the room temperature (~ 293 K), the density of helium $(0.1664 \times 10^{-3} \text{ g/cm}^3)$ is lower by one order of magnitude than that of argon $(1.663 \times 10^{-3} \text{ g/cm}^3)$, and the difference between argon and air $(1.275 \times 10^{-3} \text{ g/cm}^3)$ is relatively small [117]. The low density of helium, which creates lowest confinement among the processing environments, could explain the spherical expansion of the plasma. The particles in expanding plasma can travel further in the environment with low density. The spherical symmetry resulted from the increased degree of freedom in the radial expansion. The breakdown of environmental gases had an insignificant contribution to the emission spectra in the helium gas-streaming. The breakdown of helium was not observed, and the breakdown of nitrogen and oxygen was minimized.

Figure 83 shows the images of the laser-induced plasma in the argon gas processing condition. The largest extent in both the lateral and longitudinal directions was observed in the unfiltered image in Figure 83a. Figure 83b shows the largest bright region in the center of the irradiation spot, which indicates the most intense irradiation near the wavelength 400 nm region, among the gas processing conditions.



Figure 82. Time-integrated image of laser-induced plasma on the CVD diamond film in the helium gas-streaming; a) unfiltered image, b) image captured with BP400 filter, and c) image captured with LP525 filter.



Figure 83. Time-integrated image of laser-induced plasma on the CVD diamond film in the helium gas-streaming; a) unfiltered image, b) image captured with BP400 filter, and c) image captured with LP525 filter. As shown in Figure 83c, the extent of expanding plasma, over wavelength 525 nm, is the largest as well. The extensive plasma formation is mainly due to the breakdown of argon gas in the laser-induced plasma. The breakdown of argon results in the well-known intense argon emission spectra in the wavelength range between 700 nm \sim 1000 nm [77, 95]. As discussed in Section 5.1.6, the abundance of excited electrons, and ions from the gas breakdown also assists the C₂ Swan band emissions, which were the most intense among the gas processing conditions (see Figure 63 and Figure 64).

The environmental gas breakdown was observed not only in the argon but also in nitrogen and oxygen in ambient air (see Figure 63 and Figure 64). Even though the breakdown threshold is nearly the same between the argon and the air, the largest plasma was observed in the argon gas-streaming condition. Furthermore, the ambient air exhibited the smallest extent of plasma among the gas processing conditions. The largest extent of the plasma in the argon gas-streaming is mainly due to the very intense spectral emissions from argon and the C_2 Swan bands (see Section 5.1.7). The carbonitride formation (see Section 5.1.7) in the ambient air is mainly responsible for the smallest plasma formation. The atomic spectral intensity of argon gas was observed to be about 5 \sim 20 times larger than that for the nitrogen and oxygen. The ambient air showed the major emission spectra in the CN Violet bands, which consumed excited nitrogen particles and active carbon particles. The vigorous carbonitride formation, which caused the intense CN Violet band emission (385.09 nm ~ 388.34 nm) in the near-UV range, drastically reduced the chances for other mechanisms in the visible emissions. In the ambient air, both the C₂ Swan bands and the continuum background are the lowest among the gas processing conditions.

5.2.3-b. Effects of dynamic gas-streaming on plasma-material interaction

To examine the effects of dynamic gas-streaming on plasma-material interaction, time-integrated images of laser-induced plasma were captured from the irradiation on the thermosetting polyester resin. The polymer target has low ablation threshold (~ 0.5 J/cm^2), which is about ten times smaller than that of CVD diamond. The lower ablation threshold of polymer materials results in the higher volume-ablation rate (cm³/pulse), which gives large amount of ablated particles to form plasma. The laser irradiation on the polyester resin causes instant fragmentation of polymeric hydrocarbon (CH_x) chains, creating large plume over the irradiation spot [118]. The large plume is useful for observation of plasma dynamics in relation to the target surface. The same experimental setup and irradiation conditions, described in Section 5.2.2, were used for the timeintegrated image capturing of laser-induced plasma on the polyester resin.

Figure 84 shows the time-integrated images of laser-induced plasma on the polyester resin. To observe the extent and dynamics of expanding plasma, no optical filter was used in all of the captured images. The plasma image in the ambient air is shown in Figure 84a, which reveals the convection stream of plasma near the target surface, as indicated by the arrows. The lateral expansion, which results in the convection stream, is prominent in all of the captured images in the ambient air. Figure 84b shows the captured image in the argon gas-streaming condition. The extent of plasma expansion in the argon gas-streaming is about the same as that in the ambient air. However, the convection stream was not observed in the argon gas-streaming condition. The dynamic gas-streaming of argon influenced the expansion dynamics of the laser-induced plasma, and deterred the convection stream of plasma near the target surface.



Figure 84. Time-integrated images of laser-induced plasma on the polyester resin; a) image captured in ambient air, arrows indicate the convection stream of plasma near the target surface, b) image captured in argon gas-streaming, and c) image captured in helium gas-streaming, no optical filter was used for all captured images.



Figure 85. Laser irradiation on a leuco-dye coated paper for thermal detection around the irradiation spot; a) irradiation in the ambient air, indicating the temperature increase around the irradiation spot, b) irradiation in argon gas-streaming, and c) irradiation in helium gas-streaming.

The captured image of plasma in the helium gas-streaming condition is shown Figure 84c. The captured image in the helium gas-streaming shows the same significantly reduced extent of plasma, as compared to other gas processing conditions. Especially, the lateral expansion is drastically reduced as compared to the ambient air.

The interaction, between the convection steam of plasma and the target, is examined by the laser irradiation on the leuco-dye coated paper. A leuco-dye is an organic dye, which is colorless by chemical treatment, but it restores its color by oxidation. The oxidation is usually provided by exposure of leuco-dye molecules to air. For a thermal detector, the leuco-dye molecules are sealed in phenol-type coating. When the phenol-type coating is melted by a heat source, the leuco-dye is oxidized to restore its color, indicating its exposure to the heat.

High-density leuco-dye coated paper from Trumpf Laser is used to detect the interaction between the plasma and the target. The detection threshold of the leuco-dye

coated paper is about 100 °C. The diameter of focused laser spot was 500 μ m, and a single pulse irradiation at 3.6×10⁸ W/cm² was used for the irradiation.

Figure 85 shows the laser irradiation on a leuco-dye coated paper for thermal detection around the irradiation spot. In the ambient air (Figure 85a), the temperature increase around the irradiation spot is detected by the colorization of the leuco-dye. In contrast, the irradiation with dynamic gas-streaming conditions (Figure 85b and c) do not exhibit the colorization. No obvious difference was found in the leuco-dye detection between argon gas-streaming and helium gas-streaming. In connection to the observation in Figure 84a, it is convincing that the convection stream of plasma near the target surface causes the temperature increase around the irradiation spot. Likewise, the dynamic gas-streaming reduces the plasma-target interaction by influencing the expansion dynamics of the laser-induced plasma. The convection stream of plasma near the plasma near the target is deterred by the dynamic gas-streaming, as indicated by both the plasma image capturing and leuco-dye detection.

5.3. Chapter Summary

In this chapter, laser-induced plasma on the CVD diamond film was investigated by analytic instrumentations, such as laser-induced breakdown spectroscopy, and timeintegrated plasma image capturing. The characteristics in emission spectra, among the gas processing environments, were examined by the LIBS observations. The plasma emission spectra in the ambient air exhibited very strong CN Violet bands and the lowest C₂ Swan bands. In contrast, the argon gas-streaming shows the strongest C₂ Swan band emissions with significantly reduced CN Violet bands. The helium gas processing condition shows the lowest CN Violet band emissions with higher C₂ Swan bands than those of ambient air. As compared to the molecular spectra, relatively weak emission signals of the neutral carbon, and the singly ionized atom were identified. In the observations on environmental gas breakdown, the atomic emission route of nitrogen and oxygen is supported by the absence of molecular emission spectra, and the presence of atomic emission spectra. The breakdown of argon gas was observed by the intense argon neutral emission spectra, but no indication of helium gas breakdown was observed. The mechanisms for the major spectral emissions are discussed, and most plausible mechanisms are proposed in this study. The C_2 Swan bands were appeared in emission spectra of all gas processing condition. The C₂ Swan bands resulted from relaxation of excited C_2 molecules. The dissociative recombination process of carbon clusters is proposed for the most responsible mechanism for the C₂ Swan bands. The argon gasstreaming showed the most intensive emission spectra of the Swan bands, while the ambient air showed the lowest intensities. The abundance of excited electrons, and ions

from the gas breakdown assists the C_2 Swan band emissions. The three-body process, and the charge exchange process are proposed for the additional sources for the intense Swan bands in the argon gas-streaming. The mechanism of the strong CN Violet bands in the ambient air is proposed by invoking the dissociative combination. The proposed reaction involves the generation of excited gaseous CN by dissociative combination between carbon clusters and excited neutral nitrogen atoms. The abundance of nitrogen gas, in ambient air, transformed the laser-induced carbon clusters into gaseous CN molecules, which reduced the substantial amount of laser-ablated carbon deposition around the irradiation spot. The behavior of emission spectra is observed as a function of the laser irradiance. Regardless of the gas processing environments, the measured intensities of the emission spectra, and the continuum backgrounds behaved as an exponential function of laser irradiance. The behavior of the spectral intensity is modeled by the exponential function. In the molecular emission bands, the ratios of the emission spectrum to the continuum background were decreased as the laser irradiance increased. This indicates the substantial increase, in continuum background emission, in high laser irradiance as compared to the molecular emission spectra. In contrast, the ratio of atomic carbon emission spectrum to the continuum background was increased with an increase in the laser irradiance. The increasing ratio indicates the active ionization of carbon atoms in higher energy laser irradiance region. The excitation temperatures of the plasma are deduced by the Boltzmann-plot method in which LTE of the plasma was assumed. The plasma in LTE follows the Boltzmann distribution of electronic states of atoms and molecules. The excitation temperatures are calculated by emission intensity ratios from different upper energy levels of an element in the same electronic state. The plasma in ambient air showed the highest excitation temperature profile, while the argon gasstreaming showed the lowest profile. Electron densities are calculated from the proportionality between the Stark effect on the line broadening and the electron population. The calculated electron densities in various gas processing conditions are presented as a function of the laser irradiance. In the given range of the laser irradiance, all gas processing conditions exhibited an increase in the electron densities as the laser irradiance increased. The densest population of electrons was found in the density profile of the ambient air. The argon gas-streaming showed the lowest density profile among the processing conditions.

Time-integrated images, in the ambient air showed the lowest longitudinal expansion of the plasma. In contrast, the lateral expansion of the plasma is relatively strong. The lateral expansion is prominent in ambient air, which showed the hottest and densest plasma among the gas processing conditions. The plasma images for the helium gas processing showed more spherical-type expansion than that for the other gas processing conditions. The low density of helium, which creates lowest confinement among the processing environments, could explain the spherical expansion of the plasma. The largest extent of the plasma, in both the lateral and longitudinal directions, was observed in the argon gas-streaming. The largest extent of the plasma in the argon gas-streaming. The largest extent of the plasma in the argon gas-streaming. The largest extent of the plasma in the argon gas-streaming is mainly due to the very intense spectral emissions from argon and the C_2 Swan bands. The carbonitride formation in the ambient air is mainly responsible for the smallest plasma formation.

Chapter VI

FABRICATION OF MICRO-COMPONENTS ON CVD DIAMOND FILMS

6.1. Maskless Patterning on CVD Diamond Films

For ultra-hard film materials, such as CVD diamond, conventional machining and lithography-based patterning are difficult due to the high wear resistance and the chemical inertness [3, 4, 41]. Nevertheless, superior material properties of the diamond bring about their increasing use in various engineering applications, such as semiconductor devices, sensors and microelectromechanical systems (MEMS) [16, 18, 20, 22, 23]. Furthermore, continuous developments in growth technologies, for larger areas and low production costs, accelerate demands for diamond-based applications. Patterning and micromachining of the diamond film is a primary requirement to properly modify a film surface for the applications. Lithography-patterned diamond growth has been practiced for this purpose [54-57]. In the process, a lithography-patterned photoresist layer, in which diamond seeds are embedded, is placed in CVD reactor for the diamond growth. Besides its step-intensive procedure, the process exhibits lateral growth of diamond film, which limits the resolution and aspect ratio of a patterned structure.

Pulsed laser ablation has proven for vaporizing film materials to make patterned structures and micro-components. The laser ablation is a direct process that requires only proper arrangement of optics to control the laser beam. The CVD diamond films have been processed by various types of pulsed lasers, which have shown their capabilities in polishing, etching, and patterning [14, 16-18, 20-23, 119]. However, the patterning and

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micromachining of the film were limited due the lack of versatility of the process. The accuracy of the process was limited by the plasma-induced damage as well. In this study, for solutions to these problems, the maskless patterning system was invented with the dynamic gas streaming on the irradiation. The effects of the dynamic gas streaming were discussed in Chapter 4 and 5. The innovative maskless patterning technique employs pulsed irradiation of focused laser beam on a target material, which is translated to the programmed positions by the micro-CNC. Along with its advantages of a simple setup and a direct process, the maskless process makes a rapid prototyping possible for patterns on ultra-hard film materials [120, 121].

6.1.1. Maskless patterning versus lithography-based patterning

The comparison between the processing steps of the maskless ablation technique and the lithography-based technique is shown in Figure 86. The maskless ablation technique utilizes a stationary laser beam on a translating target material. The stationary laser spot is formed by an aperture and two convex lenses. The size of the laser spot is determined by the diameter of the aperture and the demagnification ratio of the optics. The translation of the micro-CNC stage can be programmed by a computer for any complex movements. Details about the maskless patterning system are discussed in Chapter 3. The direct ablation on the translating target can rapidly create a pattern on the diamond film, as shown in Figure 86a. In contrast, as shown in Figure 86b, the lithography-based patterning on the diamond film requires the lithography with a patterned mask on the diamond seeded photoresist layer.



Figure 86. Comparison of the processing steps between; a) the maskless ablation technique, and b) the lithography-based patterning

The lithography is followed by the selective etching for the designed pattern. Then, the diamond-seeded pattern is placed in the CVD reactor for the selective diamond growth on the patterned area. The lithography-based patterning is not only a stepintensive process but also a low-resolution process. The diamond growth on the diamond-seeded pattern proceeds to not only longitudinal directions but also lateral directions. The excessive lateral growth spoils the resolution of the pattern, which is important for the patterning of integrated features on the diamond film. Figure 87 shows the lithography-based patterned sensor (thermistor), grown from the diamond-seeded photoresist layer. As illustrated in Figure 87d, the lateral growth on the edge of the pattern is prominent in Figure 87b and c.

The CVD diamond film has great potential for the sensors, such as pressure sensors, thermistors and photodetectors.



Figure 87. Diamond growth on the diamond-seeded photoresist layer showing lateral growth; a) the CVD diamond sensor (thermistor) by the lithography-based patterning, b) resolution on its edge, c) lateral growth in the reactor and d) illustration for the diamond growth.



Figure 88. Drawing scheme, *i.e.*, translation scheme for the micro-CNC stage, for the maskless patterning on CVD diamond film.

The application of the CVD diamond film to the micro-sensors usually requires the isolated-cell patterning for electrical wiring. A pattern on a CVD diamond film is fabricated to verify the feasibility of the maskless ablation process. The average grain size and vertical thickness of the subjected diamond film (BW062) was 2 μ m and 4 μ m, respectively. The argon gas streaming at 4.72×10⁻⁴ m³/sec was used with the laser irradiance at 6×10⁸ W/cm² and the repetition rate at 10 Hz. To create a rectangular isolated-cell-pattern, a programmed translation was designed by drawing six consecutively decreasing rectangles. Figure 88 show the illustration for the drawing scheme, in which the micro-CNC stage is translated to the programmed positions.



Figure 89. Isolated cell-pattern on a CVD diamond film by the excimer laser maskless patterning process, a) the isolated cell-pattern, b) magnified view on the cell edge.

In the drawing scheme, the 250 μ m wide frame was ablated by the programmed translation with overlapping of 80 μ m diameter laser spot. The translation speed of X and Y motion stage was constant at 200 μ m/sec. The software program for the motion stage control is composed by the QuickBasic, Microsoft, and listed in Appendix A. After the ablation process, the surface was cleaned by boiling (~ 200°C) in 1:1 solution of CrO₃ and H₂SO₄ for 2 minutes.

The patterned CVD diamond film is shown in Figure 89a. The patterned cell of $550\times450 \ \mu\text{m}^2$ is isolated from its matrix. The cell-patterned CVD diamond film shows the feasibility of the maskless patterning on ultra-hard film materials. In Figure 89b, one of the cell edges is magnified to show its linearity. The roughness of the cell edges was caused by the series of pulsed irradiation with the circular spot and vibration from the micro-CNC stage. The vibration from the micro-CNC can be solved by improving the

resolution of the motion stage. The components for the high-resolution motion stage are commercially available from various sources.

6.1.2. Maskless patterning in various gas processing conditions

The maskless ablation process for the isolated-cell pattern was compared among the various gas processing conditions, such as the ambient air, the helium gas-streaming, and the argon gas-steaming. The drawing scheme, the processing parameters and the surface cleaning procedure were the same as those described in Section 6.1.1. Figure 90 shows the patterns, fabricated under the gas processing conditions. Even after the chemical cleaning for the removal of the carbon debris and amorphous graphite layers, the isolated-cell pattern processed in the ambient air in Figure 90a showed the halo-like band (indicated by the arrow) around the ablated area. No visible change was observed around the patterns processed under the helium gas-streaming (Figure 90b), and the argon gas-streaming (Figure 90c). The halo-like band, observed in the ambient air, was examined by the Raman spectroscopy (Kaiser Optical Systems, Holo Probe). The same locations in other processing conditions were examined by the Raman spectroscopy for comparison. The arrows in Figure 90 indicate the positions for the detection of the Raman spectra. Figure 91 shows the Raman spectra on the indicated positions around the cell patterns. The halo-like band in ambient air showed a relatively small intensity in the observed range including the diamond spectrum at 1332 cm⁻¹, as compared to the argon and helium gas-streaming conditions. No significant difference was found in the Raman spectra between the helium and argon gas streaming conditions.



Figure 90. Maskless ablation process for the isolated-cell pattern in the various gas processing conditions; a) ambient air, b) helium gas streaming, and c) argon gas streaming. The arrows indicate the positions for the detection of Raman spectrum in Figure 91.



Figure 91. Raman spectra on the isolated-cell patterns, processed in the various gas processing conditions.

It is conclusive from the observations that the halo-like band in the ambient air is the plasma-affected zone (PAZ), in which the sp^3 bondings in the diamond surface might be partially transformed to sp^2 bondings. The formation of the sp^2 bondings alters the conductivity of the fabricated pattern [75], which is detrimental for the sensor applications.



Figure 92. A magnified view of a complicated patterning on the diamond film showing the emblem of the Michigan State University, the Spartan helmet and the letters, MSU.

6.1.3. Processing for complicated, and large patterns

The feasibility of the maskless processing system for large, and complicated patterns, was demonstrated on the diamond film. The average grain size and vertical thickness of the subjected diamond film (BW097) was 2 μ m, and 6 μ m, respectively. The helium gas-streaming at 4.72×10^4 m³/sec was used with the laser energy fluence at 7.2×10^8 W/cm² and the repetition rate at 10 Hz. In the drawing schemes, the translation speed of X and Y motion stage was constant at 200 μ m/sec.

Figure 92 shows the complicated patterning on the diamond film, which was engraved with the emblem of the Michigan State University, the Spartan helmet and the letters.



Figure 93. Fabrication of three isolated-cell patterning on the diamond film by the maskless ablation technique.

The spot size used for the patterning was 80 μ m. Figure 93 shows the three isolated-cell patterning in millimeter scale. The multi-cell sensors are common for the signal averaging and multifunctional censors [122]. Three 1×1.5 mm² cells were ablated by the programmed translation with overlapping of 175 μ m diameter laser spot. The software programs, written by the QuickBasic, for the patterns are listed in Appendices B and C. These complicated patterns in millimeter scale verify the versatility of the patterning and the capability of the rapid prototyping for the MP-I maskless patterning system in this study.

6.1.4. Fabrication of diamond lens by maskless patterning process

Diamond has great potential for the application to the optical and x-ray windows due its excellent transparency to the electromagnetic waves [3, 4, 53]. The application for the windows involves micromachining of the freestanding CVD diamond films into required lens geometry.

To demonstrate the feasibility for the thick film micromachining, the 3.5 mm diameter diamond lens was fabricated by the maskless patterning system. The freestanding thick CVD diamond film (ST204), average thickness 270 µm, and average grain size 40 μ m, was used to fabricate the circular diamond lens. The substrate side of the freestanding diamond film, which retained flatness similar to the polished silicon wafer, was exposed to the laser irradiation. The ablation process was performed in the ambient air with the laser irradiance at 7.2×10^8 W/cm² and pulse repletion rate at 10 Hz. The spot size used for the drawing circle was 175 μ m, and the micro-CNC was programmed for the continuous circular movement. The software programs, written by the QuickBasic, for the circular pattern is listed in Appendix D. The cutting of the thick diamond film for the lens required 1.74×10^5 laser pulses, which took 4.8 hours of the Figure 94 shows the diamond lens fabricated by the maskless laser irradiations. patterning system. The patterned-cut diamond lens is shown in Figure 94a, in which the substrate side of the diamond lens is exhibited. The other side of the lens, *i.e.*, the side with the polycrystalline diamond growth, retains the same roughness as the diamond film. Figure 94b shows the smooth surface of the circular lens and the ablation-cut hole in its matrix. Figure 94c presents the micromachined edge of the lens, which shows the cleancut by the laser ablation.

The diamond lens in square geometry was also demonstrated by the maskless patterned cut. The freestanding CVD diamond film (ST235), average thickness 110 μ m and average grain size 50 μ m, was used to fabricate the square diamond lens.



Figure 94. Fabrication of the CVD diamond lens from the thick film micromachining by the maskless patterning system; a) 3.5 mm diameter diamond lens cut from the freestanding diamond film, b) the diamond lens, c) cutting edge of the lens.



Figure 95. Square patterned-cut diamond lens which is placed over the laser cut hole.

The micro-CNC was programmed for the continuous square movement. The software programs, written by the QuickBasic, for the square pattern is listed in Appendix E. All other processing parameters were the same as the circular diamond lens process. Figure 95 show the 3×3 mm² patterned-cut diamond lens, in which the side with the diamond growth was exhibited. The square lens was displayed over the laser cut hole in the matrix. The number of laser pulses required for the square patterned cutting was 6.1×10^4 pulses, which needed 1.7 hour of the laser irradiations.

6.1.5. Contour patterning on CVD Diamond Films

Contour patterning is one of the hardest patterning techniques in the lithographybased processing. In the MP-I maskless patterning system, the rotate and tilt stages allow the target translation in 3 dimensional directions. The proper alignment with the incident laser pulses makes the contour patterning possible in our MP-I system.

To demonstrate the feasibility for the contour patterning, the circular contourtrack was fabricated by the maskless patterning system. The freestanding thick CVD diamond film (ST204), average thickness 270 µm and average grain size 40 µm, was used to pattern the contour-track. The substrate side of the freestanding diamond film, which retained flatness similar to the polished silicon wafer, was exposed to the laser irradiation. The ablation process was performed in the ambient air with the laser irradiance at 7.2×10^8 W/cm² and pulse repletion rate at 10 Hz. The translation speed of the rotation stage was 11 °/sec. The software programs, written by the QuickBasic, for the pattern is listed in Appendix F. The contour patterning took 1.2×10^4 laser pulses, was used with the rotation and tilt stages. The drawing scheme for the circular contourtrack is shown in Figure 96. The target normal was tilted by 40° degrees towards the direction for the incident laser beam. The angular irradiation on the tilted specimen creates the inhomogeneous ablation depth across the spot size, as shown in the inset of Figure 96. The depth ablation rate is gradually changed from larger, in the upper region the laser spot, to smaller in the lower region of the laser spot. The inhomogeneous ablation with rotation of the specimen results in the circular concave tack on the freestanding diamond film. Figure 97a shows the overview of the circular contour-tack, which exhibits the consistent contour pattern with good symmetry. The area around the center edge is magnified in Figure 97b, which shows roughness of the laser ablated area.



Figure 96. Schematic diagram for the patterning of the circular contour track, using rotation and tilt stages.



Figure 97. Circular contour-track on the freestanding diamond film by using rotation and tilt stages; a) overview of the circular contour-track, and b) magnified view of the edge area.

6.2. Chapter Summary

The conventional machining and lithography-based patterning on the CVD diamond film are difficult due to the high wear resistance and the chemical inertness. The innovative maskless patterning technique, developed in this work, employs pulsed irradiation of focused laser beam on a target material, which is translated to the programmed positions by the micro-CNC. To produce micro patterns and structures using laser ablation, the MP-I maskless patterning system has been constructed in the High Energy Laser Processing Laboratory at MSU. Using maskless patterning system, micropatterns can be developed on diamond films through the direct ablation without masking technique. In this chapter, the feasibility of the maskless patterning on the CVD diamond film was clearly demonstrated. The demonstration includes the fabrication of the isolated-cell patterns, and the patterned engravings of MSU and its emblem on diamond films. The patterned cut for diamond windows, and the contour patterning shows extensive capabilities of the MP-I system. The maskless patterning, developed in this study, has great potential to introduce the CVD diamond film to the various applications, such as semiconductor devices, sensors, optical windows and microelectromechanical systems (MEMS). This maskless patterning addresses the current process-intensive, lithography-based patterning. Along with its advantages of a simple setup and a direct process, the maskless process makes the rapid prototyping possible for patterns on the CVD diamond film.

Chapter VII

CONCLUSION

The excellent mechanical and electrical properties make CVD diamond films uniquely qualified for the applications, such as integrated circuits, sensors, optical windows and MEMS. To utilize the excellent properties of the diamond films in the applications, micromachining and patterning of diamond films are primarily required. The excimer lasers have shown their capabilities in polishing, etching, and patterning of CVD diamond film. However, the processes have exhibited some damage, which has been obstacle to the application of laser ablation process to CVD diamond.

To overcome current barriers of the laser ablation process on CVD diamond, technical and fundamental investigations were performed in this study. In this respect, this study mainly focuses on i) macroscopic and microscopic analysis of laser-diamond coupling, and ii) analysis on the laser-induced plasma and its interaction to surrounding. These fundamental aspects in this study were linked to practical fabrication of patterned diamond components by the innovative maskless patterning technique.

The laser-diamond interaction was examined by subjecting the diamond film under three different processing environments, such as the ambient air, the vacuum condition and the gas-streaming conditions. By the dissipation of the high temperature plasma off from the surface, the inert gas-streaming showed a good feasibility for the precise micromachining of diamond films. The ablation rate of the CVD diamond film was obtained by measuring the ablation depth as a function of the number of laser pulses and the laser irradiance. The measured ablation rates were compared among the gas processing conditions, such as the ambient air, helium gas and argon gas, respectively. No significant difference was found on the ablation rate among the gas processing environments. Approximately a linear relationship was observed between the ablation depth and the number of laser pulses, and between the ablation depth and the laser irradiance. Based on these observations, linear and nonlinear models for the ablation process were proposed. The nonlinear model accounted for the divergence of the focused laser beam, and resultant decrease in the laser irradiance. The nonlinear modeling proposed the number of the laser pulses as the third order polynomial function of the ablation depth.

The initial stage of the laser-diamond interaction was observed by the AFM and Raman spectroscopy. It could be speculated from the AFM observation that the preferential interaction by the edge-chipping-off mechanism occurs at the very initial stage with in 1 to 2 laser pulses. Then, the successive laser irradiation reduces the surface roughness in overall smoothening-out mechanism. It was reasonably conclusive from the Raman spectroscopy observation that the laser-diamond interaction causes the formation of the graphitized surface micro-layer within a few pulsed irradiations. Then, the selfsustaining graphite layer absorbs the successive laser pulses for the ablation, and the surface morphology evolves according to the ablation.

To examine the evolution of the surface morphology beyond the initial interaction, *in-situ* observation was performed for the laser irradiation on the CVD diamond film. The sharp edges and vertexes exhibited higher etching rate than the planes

and valleys. The roughness reduction was caused by the uneven etching on the jagged polycrystalline diamond crystals. The uneven etching ratio is explained by the overheating of the crystal edges and vertexes due to the laser irradiation.

Laser-induced plasma on the CVD diamond film was investigated by analytic instrumentations, such as laser-induced breakdown spectroscopy, and time-integrated The characteristics in emission spectra, among the gas plasma image capturing. processing environments, were examined by the LIBS observations. The plasma emission spectra in the ambient air exhibited very strong CN Violet bands and the lowest C_2 Swan bands. In contrast, the argon gas-streaming shows the strongest C_2 Swan band emissions with significantly reduced CN Violet bands. The helium gas processing condition shows the lowest CN Violet band emissions with higher C₂ Swan bands than those of ambient air. As compared to the molecular spectra, relatively weak emission signals of the neutral carbon, and the singly ionized atom were identified. In the observations on environmental gas breakdown, the atomic emission route of nitrogen and oxygen is supported by the absence of molecular emission spectra, and the presence of atomic emission spectra. The breakdown of argon gas was observed by the intense argon neutral emission spectra, but no indication of helium gas breakdown was observed. The mechanisms for the major spectral emissions are discussed, and most plausible mechanisms are proposed in this study.

The excitation temperatures of the plasma are deduced by the Boltzmann-plot method in which LTE of the plasma was assumed. The excitation temperatures are calculated by emission intensity ratios from different upper energy levels of an element in the same electronic state. The plasma in ambient air showed the highest excitation temperature profile, while the argon gas-streaming showed the lowest profile. Electron densities are calculated from the proportionality between the Stark effect on the line broadening and the electron population. The calculated electron densities in various gas processing conditions are presented as a function of the laser irradiance. In the given range of the laser irradiance, all gas processing conditions exhibited an increase in the electron densities as the laser irradiance increased. The densest population of electrons was found in the density profile of the ambient air. The argon gas-streaming showed the lowest density profile among the processing conditions.

Time-integrated images, in the ambient air showed the lowest longitudinal expansion of the plasma. In contrast, the lateral expansion of the plasma is relatively strong. The lateral expansion is prominent in ambient air, which showed the hottest and densest plasma among the gas processing conditions. The plasma images for the helium gas processing showed more spherical-type expansion than that for the other gas processing conditions. The low density of helium, which creates lowest confinement among the processing environments, could explain the spherical expansion of the plasma. The largest extent of the plasma, in both the lateral and longitudinal directions, was observed in the argon gas-streaming. The largest extent of the plasma in the argon gas-streaming. The largest extent of the plasma in the argon gas-streaming is mainly due to the very intense spectral emissions from argon and the C_2 Swan bands. The carbonitride formation in the ambient air is mainly responsible for the smallest plasma formation.

The conventional machining and lithography-based patterning on the CVD diamond film are difficult due to the high wear resistance and the chemical inertness. The innovative maskless patterning technique, developed in this work, employs pulsed

irradiation of focused laser beam on a target material, which is translated to the programmed positions by the micro-CNC. To produce micro patterns and structures using laser ablation, the MP-I maskless patterning system has been constructed in the High Energy Laser Processing Laboratory at MSU. The innovative maskless patterning technique employs pulsed irradiation of a focused laser beam on a target material, which is translated to the programmed positions by a micro computer numerical controlled (micro-CNC) stage. The feasibility of the maskless patterning on the CVD diamond film was clearly demonstrated. The demonstration includes the fabrication of the isolated-cell patterns, and the patterned engravings of MSU and its emblem on diamond films. The patterned cut for diamond windows, and the contour patterning shows extensive capabilities of the MP-I system. The maskless patterning, developed in this study, has great potential to introduce the CVD diamond film to the various applications, such as semiconductor devices, sensors, optical windows and microelectromechanical systems (MEMS). This maskless patterning addresses the current process-intensive, lithographybased patterning. Along with its advantages of a simple setup and a direct process, the maskless process makes the rapid prototyping possible for patterns on the CVD diamond film. The maskless patterning introduces CVD diamond films to new area of sensors, optical windows, integrated circuits and MEMS, where extreme tolerance of a material is required.
APPENDICES

APPENDIX A

Software program for the motion stage control, composed by the QuickBasic, Microsoft.

• Isolated-cell pattern in Figure 88

'\$INCLUDE: 'IS_BC.BI' 'enables instep library '\$INCLUDE: 'QB.BI'

'Main Body CALL ischeckcard(592, checkcode%) 'checks to see if card is present IF checkcode% = 0 THEN PRINT "Card not found." END END IF CALL issetcardtype(1) 'sets the card type to QuickPhase half stepping mode CALL issetcplane(1, 2) 'defines x and y axes for drawing arcs sf = 10'sets size factor CALL ispowerinit(10) 'sets power level (to 20%) 'speed in steps per second speed% = 50'delay% = 2000000 / speed% 'calculates delay between steps for speed setting CALL issetspeed(32767) 'sets stepper motor speed to min. steps per second CALL issetmode(0) 'sets motion stage to relative mode **PRINT "Starting Movement"** CALL issetspeed(2000) 'shutter speed CALL ismover(0, 0, -365, 0, exitcode%)'open shutter CALL issetspeed(32767) 'drawing speed FOR c = 0 TO 4CALL ismover(0, -(24 - 2 * c) * sf, 0, 0, exitcode%) CALL ismover((22 - 2 * c) * sf, 0, 0, 0, exitcode%) CALL ismover(0, (24 - 2 * c) * sf, 0, 0, exitcode%) CALL ismover(-(22 - 2 * c) * sf. 0, 0, 0, exitcode%) IF c <> 4 THEN CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%) NEXT c CALL issetspeed(2000) 'shutter speed CALL ismover(0, 0, 365, 0, exitcode%)'closes shutter PRINT "Block Drawn" CALL issetspeed(20000) 'spacing speed CALL ismover(-4 * sf, 4 * sf, 0, 0, exitcode%) PRINT "Program Done" END

APPENDIX B

Software program for the motion stage control, composed by the QuickBasic, Microsoft.

• MSU and its emblem (Sparty helmet) in Figure 92

```
DECLARE SUB cap (sf!, delay%)
DECLARE SUB support (sf!, delay%)
DECLARE SUB plume (sf!, delay%)
DECLARE SUB closeshutter (delay%)
DECLARE SUB openshutter (delay%)
'$INCLUDE: 'IS_BC.BI' 'enables instep library
'$INCLUDE: 'QB.BI'
'Main Body
a = 1
b = 1
WHILE a = 1
CALL ischeckcard(592, checkcode%) 'checks to see if card is present
IF checkcode% = 0 THEN
       PRINT "Card not found."
       INPUT "Do you wish to try again (1=yes,0=no)"; b
ELSE a = 0
END IF
IF b = 0 THEN a = 0
WEND
IF b = 0 THEN END
CALL issetcardtype(1) 'sets the card type to QuickPhase half stepping mode
CALL issetcplane(1, 2) 'defines x and y axes for drawing arcs
sf = 12
               'sets size factor
CALL ispowerinit(10) 'sets power level (to 20%)
'speed% is speed in steps per second
'delay% = 2000000 / speed% 'calculates delay between steps for speed setting
delav% = 32767
CALL issetspeed(delay%) 'sets stepper motor speed to speed steps per second
                    'sets motion stage to relative mode
CALL issetmode(0)
PRINT "Starting Movement"
CALL plume(sf, delay%)
CALL issetspeed(20000) 'sets to spacing speed
CALL ismover(13 * sf, -28 * sf, 0, 0, exitcode%)
CALL support(sf, delay%)
CALL ismover(1 * sf, 3 * sf, 0, 0, exitcode%)
CALL cap(sf. delav%)
PRINT "Returning to Original Position"
CALL ismover(-45 * sf, 49 * sf, 0, 0, exitcode%)
SUB cap (sf, delay%)
```

CALL openshutter(delav%)

CALL ismover(1 * sf, 0, 0, 0, exitcode%)

CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(5 * sf, 0, 0, 0, exitcode%) 'to b CALL ismover(4 * sf, 1 * sf, 0, 0, exitcode%) CALL ismover(2 * sf, 1 * sf, 0, 0, exitcode%) CALL ismover(3 * sf. 2 * sf. 0, 0, exitcode%) 'to c CALL ismover(3 * sf, 3 * sf, 0, 0, exitcode%) CALL ismover(2 * sf, 3 * sf, 0, 0, exitcode%) CALL ismover(3 * sf, 6 * sf, 0, 0, exitcode%) CALL ismover(2 * sf, 6 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 2 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 3 * sf, 0, 0, exitcode%) CALL ismover(2 * sf, 4 * sf, 0, 0, exitcode%) CALL ismover(3 * sf, 4 * sf, 0, 0, exitcode%) CALL ismover(-4 * sf. -2 * sf. 0, 0, exitcode%) CALL ismover(-4 * sf, 0, 0, 0, exitcode%) CALL ismover(0, -8 * sf, 0, 0, exitcode%) CALL ismover(-2 * sf, -4 * sf, 0, 0, exitcode%) CALL ismover(-2 * sf, -1 * sf, 0, 0, exitcode%) 'to d CALL ismover(-1 * sf, -1 * sf, 0, 0, exitcode%) CALL ismover(-2 * sf, 0, 0, 0, exitcode%) CALL ismover(0, -1 * sf, 0, 0, exitcode%) CALL ismover(-3 * sf, 0, 0, 0, exitcode%) 'to e CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(-3 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(-2 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(-1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) 'to f CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(2 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(3 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(2 * sf, 0, 0, 0, exitcode%) 'to g CALL ismover(0, -1 * sf, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(3 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 2 * sf, 0, 0, exitcode%) CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%) CALL ismover(0, 10 * sf, 0, 0, exitcode%) 'to (64,74) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 7 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 1 * sf, 0, 0, exitcode%) CALL ismover(0, 4 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 1 * sf, 0, 0, exitcode%) CALL ismover(0, 2 * sf, 0, 0, exitcode%) 'to h CALL closeshutter(20000) CALL ismover(4 * sf, -2 * sf, 0, 0, exitcode%) 'trademark CALL openshutter(delay%) CALL ismover(1 * sf, 0, 0, 0, exitcode%)

CALL ismover(0, 2 * sf, 0, 0, exitcode%) CALL ismover(0, -2 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL closeshutter(20000) CALL ismover(1 * sf, 2 * sf, 0, 0, exitcode%) CALL openshutter(delav%) CALL ismover(0, -2 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(0, -1 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 2 * sf, 0, 0, exitcode%) CALL closeshutter(20000) 'end of trademark back to cap at h CALL ismover(-9 * sf, 0, 0, 0, exitcode%) CALL openshutter(delay%) CALL ismover(0, -1 * sf, 0, 0, exitcode%) CALL ismover(-2 * sf, 0, 0, 0, exitcode%) CALL ismover(-3 * sf, -1 * sf, 0, 0, exitcode%) CALL ismover(-4 * sf, -2 * sf, 0, 0, exitcode%) CALL ismover(-3 * sf, -2 * sf, 0, 0, exitcode%) to i CALL ismover(-4 * sf, -3 * sf, 0, 0, exitcode%) CALL ismover(-4 * sf, -4 * sf, 0, 0, exitcode%) 'to j CALL ismover(-1 * sf, -1 * sf, 0, 0, exitcode%) CALL ismover(-1 * sf, 0, 0, 0, exitcode%) CALL ismover(-4 * sf, 1 * sf, 0, 0, exitcode%) 'to k CALL ismover(-6 * sf, 0, 0, 0, exitcode%) CALL ismover(-6 * sf, 2 * sf, 0, 0, exitcode%) CALL ismover(-2 * sf, 1 * sf, 0, 0, exitcode%) CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'to l CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, -3 * sf, 0, 0, exitcode%) CALL ismover(0, -9 * sf, 0, 0, exitcode%) 'to m CALL ismover(-2 * sf, -8 * sf, 0, 0, exitcode%) CALL ismover(0, -9 * sf, 0, 0, exitcode%) 'to n CALL ismover(1 * sf, -3 * sf, 0, 0, exitcode%) CALL ismover(2 * sf, -4 * sf, 0, 0, exitcode%) 'to o CALL ismover(5 * sf, -5 * sf, 0, 0, exitcode%) CALL ismover(4 * sf, -2 * sf, 0, 0, exitcode%) CALL ismover(3 * sf, -1 * sf, 0, 0, exitcode%) CALL ismover(5 * sf, 0, 0, 0, exitcode%) CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'to (45,33) CALL closeshutter(20000) PRINT "helmet done" END SUB SUB closeshutter (delay%) CALL issetspeed(2000) 'sets shutter speed CALL ismover(0, 0, 365, 0, exitcode%) 'closes shutter CALL issetspeed(delay%) 'resets speed to previous value END SUB SUB openshutter (delay%) CALL issetspeed(2000) 'set to shutter speed

CALL ismover(0, 0, -365, 0, exitcode%) 'open shutter

CALL issetspeed(delay%) 'return speed to previous value END SUB

SUB plume (sf, delay%) CALL openshutter(delay%) CALL ismover(4 * sf, -4 * sf, 0, 0, exitcode%) 'to A 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 4 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) '2 'CALL ismover(0, -2 * sf, 0, 0, exitcode%) '3 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) '4 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) '5 'lines 1-5 could likely be replaced by CALL ismover(2 * sf, -4 * sf, 0, 0, exitcode%) 'was comment CALL ismover(0, -12 * sf, 0, 0, exitcode%) 'to B CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -4 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -4 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -4 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf. 0, 0, 0, exitcode%) CALL ismover(-4 * sf, -12 * sf, 0, 0, exitcode%) 'was added ... CALL ismover(0, -12 * sf, 0, 0, exitcode%) 'to C 'CALL ismover(0, -3 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, 2 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -3 * sf. 0, 0, exitcode%) 'to D old CALL ismover(1 * sf, -5 * sf, 0, 0, exitcode%) 'to D 'CALL ismover(0, -2 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, 1 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%) 'CALL ismover(0, -3 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, 1 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%) 'CALL ismover(0, -2 * sf, 0, 0, exitcode%) 'to E old CALL ismover(1 * sf, -4 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, -3 * sf, 0, 0, exitcode%) 'to E 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -2 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -2 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -2 * sf, 0, 0, exitcode%) FOR x = 1 TO 4

CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'NEXT 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, 1 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%) 'FOR x = 1 TO 3 CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'NEXT x 'CALL ismover(2 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'to F old CALL ismover(2 * sf, -4 * sf, 0, 0, exitcode%) CALL ismover(3 * sf, -4 * sf, 0, 0, exitcode%) CALL ismover(3 * sf, -3 * sf, 0, 0, exitcode%) CALL ismover(4 * sf, -3 * sf, 0, 0, exitcode%) CALL ismover(3 * sf, -2 * sf, 0, 0, exitcode%) 'to F 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(2 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) FOR x = 1 TO 3 CALL ismover(0, -1 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 1 * sf, 0, 0, exitcode%) CALL ismover(-1 * sf, 0, 0, 0, exitcode%) CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'NEXT x 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(3 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(4 * sf. 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'to G old CALL ismover(3 * sf, -2 * sf, 0, 0, exitcode%) CALL ismover(6 * sf, -3 * sf, 0, 0, exitcode%) CALL ismover(9 * sf, -3 * sf, 0, 0, exitcode%) 'to G 'CALL ismover(24 * sf, 0, 0, 0, exitcode%) CALL ismover(23 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, 1 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%) 'CALL ismover(4 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, 1 * sf, 0, 0, exitcode%) 'CALL ismover(3 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, 1 * sf, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'CALL ismover(1 * sf, 0, 0, 0, exitcode%) 'CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%) 'CALL ismover(3 * sf, 0, 0, 0, exitcode%)

```
'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'CALL ismover(2 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'CALL ismover(1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(-1 * sf. 1 * sf. 0, 0, exitcode%)
'CALL ismover(2 * sf, 0, 0, 0, exitcode%)
                                                 'to H old
CALL ismover(9 * sf, 3 * sf, 0, 0, exitcode%)
CALL ismover(3 * sf, 2 * sf, 0, 0, exitcode%)
                                                 'to H
CALL ismover(-7 * sf, 14 * sf, 0, 0, exitcode%)
                                                 'to I new
'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'CALL ismover(1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%)
'FOR x = 1 TO 2
      CALL ismover(0, 3 * sf, 0, 0, exitcode%)
      CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
      CALL ismover(0, -1 * sf, 0, 0, exitcode%)
      CALL ismover(1 * sf, 0, 0, 0, exitcode%)
      CALL ismover(0, 1 * sf, 0, 0, exitcode%)
      CALL ismover(-1 * sf, -1 * sf, 0, 0, exitcode%)
'NEXT x
'CALL ismover(0, 3 * sf, 0, 0, exitcode%)
'FOR x = 1 TO 3
      CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
      CALL ismover(0, 2 * sf, 0, 0, exitcode%)
'NEXT x
'CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
                                                 'to I old
CALL ismover(-2 * sf, -1 * sf, 0, 0, exitcode%)
CALL ismover(-3 * sf, -1 * sf, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'CALL ismover(-3 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'CALL ismover(-3 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'CALL ismover(-7 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'CALL ismover(1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'CALL ismover(-1 * sf, -1 * sf, 0, 0, exitcode%)
'CALL ismover(-5 * sf, 0, 0, 0, exitcode%)
                                                 'to J old
CALL ismover(-3 * sf, -1 * sf, 0, 0, exitcode%)
CALL ismover(-4 * sf, -1 * sf, 0, 0, exitcode%)
CALL ismover(-5 * sf, -1 * sf, 0, 0, exitcode%)
CALL ismover(-3 * sf, 0, 0, 0, exitcode%)
                                                'to J new
'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'CALL ismover(-8 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'CALL ismover(-4 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'CALL ismover(1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
```

```
'CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%)
FOR x = 1 TO 4
      CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
      CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'NEXT x
FOR x = 1 TO 2
      CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
      CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'NEXT x
'CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
                                                 'to K old
CALL ismover(-6 * sf, 1 * sf, 0, 0, exitcode%)
CALL ismover(-5 * sf, 1 * sf, 0, 0, exitcode%)
CALL ismover(-3 * sf, 1 * sf, 0, 0, exitcode%)
CALL ismover(-8 * sf, 4 * sf, 0, 0, exitcode%)
CALL ismover(-3 * sf, 2 * sf, 0, 0, exitcode%)
                                                'to K
FOR x = 1 TO 3
      CALL ismover(0, 1 * sf, 0, 0, exitcode%)
      CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
'NEXT x
'CALL ismover(0, 2 * sf, 0, 0, exitcode%)
'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
FOR x = 1 TO 2
      CALL ismover(0, 1 * sf, 0, 0, exitcode%)
      CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
'NEXT x
'FOR x = 1 TO 3
      CALL ismover(0, 2 * sf, 0, 0, exitcode%)
      CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
'NEXT x
'CALL ismover(0, 3 * sf, 0, 0, exitcode%)
'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
                                                 'to L old
CALL ismover(-3 * sf, 3 * sf, 0, 0, exitcode%)
CALL ismover(-3 * sf, 4 * sf, 0, 0, exitcode%)
CALL ismover(-3 * sf, 6 * sf, 0, 0, exitcode%)
CALL ismover(-1 * sf, 3 * sf, 0, 0, exitcode%)
                                                'to L
'CALL ismover(0, 4 * sf, 0, 0, exitcode%)
'CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%)
'CALL ismover(0, 5 * sf, 0, 0, exitcode%)
'CALL ismover(1 * sf, 1 * sf, 0, 0, exitcode%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'FOR x = 1 TO 3
      CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
      CALL ismover(0, -1 * sf, 0, 0, exitcode%)
      CALL ismover(1 * sf, 0, 0, 0, exitcode%)
      CALL ismover(0, -1 * sf, 0, 0, exitcode%)
'NEXT x
'CALL ismover(0, 12 * sf, 0, 0, exitcode%)
                                                 'to M old
CALL ismover(-1 * sf, 6 * sf, 0, 0, exitcode%)
CALL ismover(0, 3 * sf, 0, 0, exitcode%)
CALL ismover(1 * sf, 7 * sf, 0, 0, exitcode%)
                                                'to M
'CALL ismover(0, 3 * sf, 0, 0, exitcode%)
'CALL ismover(1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, 5 * sf, 0, 0, exitcode%)
'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(0, 7 * sf, 0, 0, exitcode%)
'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
```

```
'CALL ismover(1 * sf, 0, 0, 0, exitcode%)
        'CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%)
        'CALL ismover(0, 2 * sf, 0, 0, exitcode%)
        'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
        'CALL ismover(0, 2 * sf, 0, 0, exitcode%)
        'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
        'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
        'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
        'CALL ismover(0, 2 * sf, 0, 0, exitcode%)
        'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
        'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
        'CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
        'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
        'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
        'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
        'CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
                                                     'to (1,81) old
        CALL ismover(1 * sf, 4 * sf, 0, 0, exitcode%)
        CALL ismover(0, 3 * sf, 0, 0, exitcode%)
        CALL ismover(-1 * sf, 7 * sf, 0, 0, exitcode%)
        CALL ismover(-1 * sf, 3 * sf, 0, 0, exitcode%)
        CALL ismover(-1 * sf, 2 * sf, 0, 0, exitcode%)
        CALL ismover(-2 * sf, 3 * sf, 0, 0, exitcode%)
        CALL ismover(-3 * sf, 2 * sf, 0, 0, exitcode%)
        CALL ismover(-3 * sf, 1 * sf, 0, 0, exitcode%) 'to (1,81)
        CALL closeshutter(delay%)
        PRINT "plume done"
END SUB
SUB support (sf, delay%)
        'support 1
        CALL openshutter(delay%)
         'CALL ismover(0, -3 * sf, 0, 0, exitcode%)
         'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
         'CALL ismover(0, -5 * sf, 0, 0, exitcode%)
         'CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%)
         'CALL ismover(0, -1 * sf, 0, 0, exitcode%)
         'CALL ismover(6 * sf, 0, 0, 0, exitcode%)
         'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
         'CALL ismover(2 * sf, 0, 0, 0, exitcode%)
         'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
         'CALL ismover(-4 * sf, 0, 0, 0, exitcode%)
              FOR x = 1 TO 3
              CALL ismover(0, 1 * sf, 0, 0, exitcode%)
         .
               CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
         'NEXT x
         'CALL ismover(0, 2 * sf, 0, 0, exitcode%)
         'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
                                                      'to (14,50) old
        CALL ismover(-1 * sf, -5 * sf, 0, 0, exitcode%)
        CALL ismover(0, -1 * sf, 0, 0, exitcode%)
        CALL ismover(1 * sf, -4 * sf, 0, 0, exitcode%)
        CALL ismover(8 * sf, 1 * sf, 0, 0, exitcode%)
        CALL ismover(0, 1 * sf, 0, 0, exitcode%)
        CALL ismover(-3 * sf, 0, 0, 0, exitcode%)
        CALL ismover(-2 * sf, 1 * sf, 0, 0, exitcode%)
```

```
CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%)
```

'CALL ismover(0, -1 * sf, 0, 0, exitcode%)

```
CALL ismover(-2 * sf, 4 * sf, 0, 0, exitcode%)
CALL ismover(0, 2 * sf, 0, 0, exitcode%)
CALL closeshutter(20000)
CALL ismover(0, -3 * sf, 0, 0, exitcode%)'to original end pt. (14.50)
CALL ismover(10 * sf, -8 * sf, 0, 0, exitcode%)
CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'moved from below
'support 2
CALL openshutter(delav%)
'CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'moved to above
CALL ismover(-9 * sf, -1 * sf, 0, 0, exitcode%)
CALL ismover(1 * sf, -3 * sf, 0, 0, exitcode%)
CALL ismover(8 * sf, 4 * sf, 0, 0, exitcode%)
CALL closeshutter(20000)
CALL ismover(3 * sf, -3 * sf, 0, 0, exitcode%)
'support 3
CALL openshutter(delav%)
CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
CALL ismover(-7 * sf, -3 * sf, 0, 0, exitcode%)
CALL ismover(0, -1 * sf, 0, 0, exitcode%)
CALL ismover(2 * sf, -2 * sf, 0, 0, exitcode%)
CALL ismover(1 * sf, 0, 0, 0, exitcode%)
CALL ismover(5 * sf, 5 * sf, 0, 0, exitcode%)
CALL ismover(1 * sf, 0, 0, 0, exitcode%)
CALL ismover(0, 1 * sf. 0, 0, exitcode%)
CALL closeshutter(20000)
CALL ismover(2 * sf, -2 * sf, 0, 0, exitcode%)
'support 4
CALL openshutter(delay%)
CALL ismover(-4 * sf, -4 * sf, 0, 0, exitcode%)
CALL ismover(-3 * sf, -2 * sf, 0, 0, exitcode%)
CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
CALL ismover(0, -1 * sf, 0, 0, exitcode%)
CALL ismover(2 * sf, -2 * sf, 0, 0, exitcode%)
CALL ismover(1 * sf, 0, 0, 0, exitcode%)
CALL ismover(2 * sf, 3 * sf, 0, 0, exitcode%)
CALL ismover(4 * sf, 4 * sf, 0, 0, exitcode%)
CALL ismover(-1 * sf, 2 * sf, 0, 0, exitcode%)
CALL closeshutter(20000)
CALL ismover(4 * sf, -3 * sf, 0, 0, exitcode%)
CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'for smoothness
'support 5
CALL openshutter(delay%)
'CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'replaces last to smooth
CALL ismover(-5 * sf, -7 * sf, 0, 0, exitcode%)
CALL ismover(0, -1 * sf, 0, 0, exitcode%)
CALL ismover(2 * sf, -2 * sf, 0, 0, exitcode%)
CALL ismover(5 * sf, 8 * sf, 0, 0, exitcode%)
'CALL ismover(0, 2 * sf, 0, 0, exitcode%)
CALL ismover(0, 1 * sf, 0, 0, exitcode%) 'these two replace previous
CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%) 'line - to smooth
CALL closeshutter(20000)
CALL ismover(2 * sf, -2 * sf, 0, 0, exitcode%)
'support 6
CALL openshutter(delav%)
CALL ismover(-3 * sf, -9 * sf, 0, 0, exitcode%)
```

```
'CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(3 * sf, -1 * sf, 0, 0, exitcode%)
CALL ismover(2 * sf, -1 * sf, 0, 0, exitcode%) 'replaces last two
CALL ismover(1 * sf, 1 * sf, 0, 0, exitcode%)
CALL ismover(2 * sf. 8 * sf. 0, 0, exitcode%)
'CALL ismover(0, 1 * sf, 0, 0, exitcode%)
'CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
CALL ismover(-2 * sf, 1 * sf, 0, 0, exitcode%) 'combines last two
CALL closeshutter(20000)
CALL ismover(6 * sf, -1 * sf, 0, 0, exitcode%)
'support 7
CALL openshutter(delay%)
CALL ismover(-1 * sf, 0, 0, 0, exitcode%)
'CALL ismover(-1 * sf, -1 * sf, 0, 0, exitcode%)
CALL ismover(-1 * sf, 0, 0, 0, exitcode%) 'previous line as two
CALL ismover(0, -1 * sf, 0, 0, exitcode%) 'lines instead of one
CALL ismover(-2 * sf, -8 * sf, 0, 0, exitcode%)
CALL ismover(0, -1 * sf, 0, 0, exitcode%)
CALL ismover(4 * sf, -1 * sf, 0, 0, exitcode%)
CALL ismover(0, 11 * sf, 0, 0, exitcode%)
CALL closeshutter(20000)
CALL ismover(3 * sf, 0, 0, 0, exitcode%)
'support 8
CALL openshutter(delay%)
CALL ismover(0, -11 * sf, 0, 0, exitcode%)
CALL ismover(7 * sf, 0, 0, 0, exitcode%)
CALL ismover(4 * sf, 1 * sf, 0, 0, exitcode%)
CALL ismover(2 * sf, 0, 0, 0, exitcode%)
CALL ismover(-2 * sf, 0, 0, 0, exitcode%)
CALL ismover(-3 * sf, 1 * sf, 0, 0, exitcode%)
CALL ismover(-4 * sf, 2 * sf, 0, 0, exitcode%)
CALL ismover(-1 * sf, 1 * sf, 0, 0, exitcode%)
CALL ismover(-1 * sf, 2 * sf, 0, 0, exitcode%)
CALL ismover(-2 * sf, 4 * sf, 0, 0, exitcode%) 'to (44,30)
CALL closeshutter(20000)
PRINT "supports done"
```

END SUB

DECLARE SUB checkexit (exitcode%) DECLARE SUB drawM (sf!) 'draws the letter M by moving surface DECLARE SUB spaceletter (sf!) 'switches from M to S or S to U DECLARE SUB drawS (sf!) 'draws the letter S by moving surface DECLARE SUB drawU (sf!) 'draws the letter U by moving surface '\$INCLUDE: 'IS_BC.BI' 'enables instep library '\$INCLUDE: 'QB.BI' 'Main Body a = 1 b = 1WHILE a = 1CALL ischeckcard(592, checkcode%) 'checks to see if card is present IF checkcode% = 0 THEN PRINT "Card not found." INPUT "Do you wish to try again (1=ves.0=no)": b ELSE a = 0END IF IF b = 0 THEN a = 0WEND IF b = 0 THEN END 'INPUT "Do you wish to end on movement errors (1=ves, 0=no)? ", eoe% 'I may eventually put in this option, but eee% must then be passed to each 'letter's subroutine. CALL issetcardtype(1) 'sets the card type to QuickPhase half stepping mode CALL issetcplane(1, 2) 'defines x and y axes for drawing arcs 'sets size factor sf = 50CALL ispowerinit(10) 'sets power level (to 20%) speed% is speed in steps per second 'delay% = 2000000 / speed% 'calculates delay between steps for speed setting CALL issetspeed(32767) 'sets stepper motor speed to speed steps per second CALL issetmode(0) 'sets motion stage to relative mode **PRINT "Starting Movement"** CALL drawM(sf) CALL spaceletter(sf) CALL drawS(sf) CALL spaceletter(sf) CALL drawU(sf) INPUT "Return to Starting Position (1=ves, 0=no)?", origin CALL issetspeed(20000) 'sets speed to 100 steps/sec IF origin = 1 THEN CALL ismover(-26 * sf, 0, 0, 0, exitcode%) END

SUB checkexit (exitcode%) 'Add parameter eoe% for End On Error option IF NOT exitcode% = 0 THEN SELECT CASE exitcode% CASE exitcode% = 1 TO 2 PRINT "Limit Switch Encountered - M1" CASE exitcode% = 3 TO 4 PRINT "Limit Switch Encountered - M2" CASE exitcode% = 5 TO 6 PRINT "Limit Switch Encountered - M3" CASE exitcode% = 7 TO 8

PRINT "Limit Switch Encountered - M4" CASE exitcode% = 32PRINT "Encoder Error on M1" CASE exitcode% = 33PRINT "Encoder Error on M2" CASE exitcode% = 34 PRINT "Encoder Error on M3" CASE exitcode% = 35PRINT "Encoder Error on M4" CASE exitcode% = 51**PRINT "Shield Open"** CASE exitcode% = 129 PRINT "Keyboard Abort (ESC)" CASE exitcode% = 185 PRINT "Keyboard Pause (spacebar)" CASE ELSE PRINT "Move Unsuccessful - Reason Unknown" **END SELECT** 'IF eoe% = 1 THEN END

END IF END SUB

SUB drawM (sf)

CALL issetspeed(2000000 / 1000) 'sets speed to 1000 steps/sec CALL ismover(0, 0, -365, 0, exitcode%) 'unblocks laser IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL issetspeed(32767) 'returns to writing speed CALL ismover(0, -8 * sf, 0, 0, exitcode%) 'first lea of M IF exitcode THEN CALL checkexit(exitcode%) 'error check CALL ismover(3 * sf, 4 * sf, 0, 0, exitcode%) 'down to middle of M IF exitcode THEN CALL checkexit(exitcode%) 'error check CALL ismover(3 * sf, -4 * sf, 0, 0, exitcode%) 'up from middle of M IF exitcode THEN CALL checkexit(exitcode%) 'error check CALL ismover(0, 8 * sf, 0, 0, exitcode%) 'last leg of M IF exitcode THEN CALL checkexit(exitcode%) 'error check CALL issetspeed(2000) 'sets speed to 1000 steps/sec CALL ismover(0, 0, 365, 0, exitcode%) 'blocks laser IF exitcode THEN CALL checkexit(exitcode%) 'error check

END SUB

SUB drawS (sf)

CALL issetspeed(2000) 'sets speed to 1000 steps/sec CALL ismover(0, 0, -365, 0, exitcode%) 'unblocks laser IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL issetspeed(32767) 'resets to writing speed CALL isarc(2 * sf, 0, 2 * sf, -2 * sf, 1, exitcode%) 'bottom of S IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL isarc(0, -2 * sf, 2 * sf, -2 * sf, -1, exitcode%) 'top of S IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL issetspeed(2000) 'sets speed to 1000 steps/sec CALL ismover(0, 0, 365, 0, exitcode%) 'blocks laser IF exitcode% THEN CALL checkexit(exitcode%) 'error check

END SUB

SUB drawU (sf)

CALL issetspeed(2000) 'sets speed to 1000 steps/sec

CALL ismover(0, 0, -365, 0, exitcode%) 'unblocks laser IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL issetspeed(32767) 'resets to writing speed CALL ismover(0, 6 * sf, 0, 0, exitcode%) left line of U IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL isarc(2 * sf, 0, 4 * sf, 0, 1, exitcode%) bottom of U IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL ismover(0, -6 * sf, 0, 0, exitcode%) 'right line of U IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL ismover(0, 6 * sf, 0, 0, exitcode%) 'positioning step IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL isarc(2 * sf, 0, 2 * sf, 2 * sf, 1, exitcode%) 'tail of U IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL issetspeed(2000) 'sets speed to shutter speed CALL ismover(0, 0, 365, 0, exitcode%) 'blocks laser IF exitcode% THEN CALL checkexit(exitcode%) 'error check END SUB

SUB spaceletter (sf)

CALL issetspeed(20000) 'sets speed to 100 steps/sec CALL ismover(5 * sf, -2 * sf, 0, 0, exitcode%) 'move to next letter IF exitcode% THEN checkexit (exitcode%) 'error check END SUB

APPENDIX C

Software program for the motion stage control, composed by the QuickBasic, Microsoft.

• Three isolated-cell pattern in Figure 93

```
DECLARE SUB checkexit (exitcode%)
DECLARE SUB outerblock (sf!)
DECLARE SUB innerblocks (sf!)
$INCLUDE: 'IS_BC.BI' 'enables instep library
'$INCLUDE: 'QB.BI'
'Main Body
CALL ischeckcard(592, checkcode%) 'checks to see if card is present
IF checkcode% = 0 THEN
       PRINT "Card not found."
       END
END IF
'INPUT "Do you wish to end on movement errors (1=yes, 0=no)? ", eoe%
'I may eventually put in this option, but ece% must then be passed to each
'letter's subroutine.
CALL issetcardtype(1) 'sets the card type to QuickPhase half stepping mode
CALL issetcplane(1, 2) 'defines x and y axes for drawing arcs
sf = 50
                'sets size factor
CALL ispowerinit(10) 'sets power level (to 20%)
                    'speed in steps per second
speed% = 50
'delay% = 2000000 / speed% 'calculates delay between steps for speed setting
CALL issetspeed(32767) 'sets stepper motor speed to speed steps per second
                    'sets motion stage to relative mode
CALL issetmode(0)
PRINT "Starting Movement"
CALL outerblock(sf)
CALL innerblocks(sf)
PRINT "Test Pattern Drawn."
PRINT "Returning to original position"
CALL issetspeed(20000) 'sets to spacing speed
CALL ismover(-18 * sf, 2 * sf, 0, 0, exitcode%)'returns to original position
END
SUB checkexit (exitcode%) 'Add parameter eoe% for End On Error option
        IF NOT exitcode% = 0 THEN
               SELECT CASE exitcode%
                       CASE exitcode% = 1 TO 2
                               PRINT "Limit Switch Encountered - M1"
                       CASE exitcode% = 3 TO 4
                               PRINT "Limit Switch Encountered - M2"
                       CASE exitcode\% = 5 \text{ TO } 6
                               PRINT "Limit Switch Encountered - M3"
                       CASE exitcode% = 7 TO 8
                               PRINT "Limit Switch Encountered - M4"
                       CASE exitcode\% = 32
                               PRINT "Encoder Error on M1"
```

CASE exitcode% = 33PRINT "Encoder Error on M2" CASE exitcode% = 34 PRINT "Encoder Error on M3" CASE exitcode% = 35PRINT "Encoder Error on M4" CASE exitcode% = 51**PRINT "Shield Open"** CASE exitcode% = 129 PRINT "Keyboard Abort (ESC)" CASE exitcode% = 185 PRINT "Keyboard Pause (spacebar)" CASE ELSE PRINT "Move Unsuccessful - Reason Unknown" END SELECT 'IF eoe% = 1 THEN END **END IF**

END SUB

SUB innerblocks (sf)

CALL issetspeed(20000) 'set speed to spacing speed CALL ismover(6 * sf, 0, 0, 0, exitcode%) CALL issetspeed(2000) 'sets to shutter speed CALL ismover(0, 0, -365, 0, exitcode%)'opens shutter CALL issetspeed(32767) 'sets speed to drawing speed CALL ismover(0, -9 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 10 * sf, 0, 0, exitcode%) CALL ismover(1 * sf. 0, 0, 0, exitcode%) CALL ismover(0, -9 * sf, 0, 0, exitcode%) CALL issetspeed(2000) 'set to shutter speed CALL ismover(0, 0, 365, 0, exitcode%) 'closes shutter CALL issetspeed(20000) 'set to spacing speed CALL ismover(6 * sf, 0, 0, 0, exitcode%) CALL issetspeed(2000) 'set to shutter speed CALL ismover(0, 0, -365, 0, exitcode%) 'opens shutter CALL issetspeed(32767) 'set to drawing speed CALL ismover(0, 9 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, -10 * sf, 0, 0, exitcode%) CALL ismover(1 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 9 * sf, 0, 0, exitcode%) 'inner blocks done CALL issetspeed(2000) 'set to shutter speed CALL ismover(0, 0, 365, 0, exitcode%) 'closes shutter

END SUB

SUB outerblock (sf) CALL issetspeed(2000) 'sets speed to 1000 steps/sec CALL ismover(0, 0, -365, 0, exitcode%) 'opens shutter CALL issetspeed(32767) 'sets speed to drawing speed CALL ismover(0, -12 * sf, 0, 0, exitcode%) CALL ismover(26 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 12 * sf, 0, 0, exitcode%) CALL ismover(-26 * sf, 0, 0, 0, exitcode%) 'if we want to change the spot size or the size of the pattern, 215

'a for next loop will need to be included for this next part CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%) CALL ismover(0, -10 * sf, 0, 0, exitcode%) CALL ismover(24 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 10 * sf, 0, 0, exitcode%) CALL ismover(-24 * sf, 0, 0, 0, exitcode%) CALL ismover(1 * sf, -1 * sf, 0, 0, exitcode%) CALL ismover(0, -8 * sf, 0, 0, exitcode%) CALL ismover(22 * sf, 0, 0, 0, exitcode%) CALL ismover(22 * sf, 0, 0, 0, exitcode%) CALL ismover(-22 * sf, 0, 0, 0, exitcode%) CALL ismover(0, 0, 365, 0, exitcode%) 'closes shutter

END SUB

APPENDIX D

DECLARE SUB checkexit (exitcode%)

Software program for the motion stage control, composed by the QuickBasic, Microsoft.

• Patterned cut for the circular lens in Figure 94

```
DECLARE SUB drawO (sfl) 'draws the circle moving surface
'$INCLUDE: 'IS_BC.BI' 'enables instep library
'$INCLUDE: 'QB.BI'
'Main Body
a = 1
b = 1
WHILE a = 1
CALL ischeckcard(592, checkcode%) 'checks to see if card is present
IF checkcode% = 0 THEN
       PRINT "Card not found."
       INPUT "Do you wish to try again (1=yes,0=no)"; b
ELSE a = 0
END IF
IF b = 0 THEN a = 0
WEND
IF b = 0 THEN END
CALL issetcardtype(1) 'sets the card type to QuickPhase half stepping mode
CALL issetcplane(1, 2) 'defines x and y axes for drawing arcs
sf = 150
                 'sets size factor
CALL ispowerinit(10) 'sets power level (to 20%)
speed% is speed in steps per second
'delay% = 2000000 / speed% 'calculates delay between steps for speed setting
CALL issetspeed(32767) 'sets stepper motor speed to speed steps per second
CALL issetmode(0) 'sets motion stage to relative mode
PRINT "Starting Movement"
CALL issetspeed(2000000 / 1000) 'sets speed to 1000 steps/sec
CALL ismover(0, 0, -365, 0, exitcode%)
                                         'unblocks laser
IF exitcode% THEN CALL checkexit(exitcode%) 'error check
CALL issetspeed(32767)
                              'returns to writing speed
INPUT "How many repetitions do you want?", x
FOR N = 1 TO x
        CALL drawO(sf)
NEXT N
CALL issetspeed(2000000 / 1000) 'sets speed to 1000 steps/sec
CALL ismover(0, 0, 365, 0, exitcode%)
                                           'blocks laser
IF exitcode THEN CALL checkexit(exitcode%) 'error check
```

```
INPUT "Return to Starting Position (1=yes, 0=no)? ", origin
CALL issetspeed(20000) 'sets speed to 100 steps/sec
IF origin = 1 THEN CALL ismover(0, 0, 0, 0, exitcode%)
END
SUB checkexit (exitcode%) 'Add parameter eoe% for End On Error option
        IF NOT exitcode% = 0 THEN
               SELECT CASE exitcode%
                       CASE exitcode% = 1 TO 2
                              PRINT "Limit Switch Encountered - M1"
                       CASE exitcode\% = 3 TO 4
                              PRINT "Limit Switch Encountered - M2"
                       CASE exitcode% = 5 TO 6
                              PRINT "Limit Switch Encountered - M3"
                       CASE exitcode% = 7 TO 8
                              PRINT "Limit Switch Encountered - M4"
                       CASE exitcode\% = 32
                              PRINT "Encoder Error on M1"
                       CASE exitcode% = 33
                              PRINT "Encoder Error on M2"
                       CASE exitcode% = 34
                              PRINT "Encoder Error on M3"
                       CASE exitcode% = 35
                              PRINT "Encoder Error on M4"
                       CASE exitcode% = 51
                              PRINT "Shield Open"
                       CASE exitcode% = 129
                              PRINT "Keyboard Abort (ESC)"
                       CASE exitcode% = 185
                              PRINT "Keyboard Pause (spacebar)"
                      CASE ELSE
                              PRINT "Move Unsuccessful - Reason Unknown"
               END SELECT
               'IF eoe% = 1 THEN END
       END IF
END SUB
SUB drawO (sf!)
       centerx& = -3 * sf: centery& = 0 'select a start point
       Xdest& = 0: Ydest& = 0
                                 'full circle
       dir% = 1
                           'clockwise rotation
       CALL isarc(centerx&, centery&, Xdest&, Ydest&, dir%, exitcode%)
END SUB
```

APPENDIX E

Software program for the motion stage control, composed by the QuickBasic, Microsoft.

• Patterned cut for the square lens in Figure 95

DECLARE SUB checkexit (exitcode%) DECLARE SUB drawSQ (sf!) 'draws the letter M by moving surface '\$INCLUDE: 'IS_BC.BI' 'enables instep library '\$INCLUDE: 'QB.BI' 'Main Body a = 1 b = 1WHILE a = 1CALL ischeckcard(592, checkcode%) 'checks to see if card is present IF checkcode% = 0 THEN PRINT "Card not found." INPUT "Do you wish to try again (1=yes,0=no)"; b ELSE a = 0END IF IF b = 0 THEN a = 0WEND IF b = 0 THEN END 'INPUT "Do you wish to end on movement errors (1=yes, 0=no)? ", eoe%

'I may eventually put in this option, but eoe% must then be passed to each 'letter's subroutine.
CALL issetcardtype(1) 'sets the card type to QuickPhase half stepping mode CALL issetcplane(1, 2) 'defines x and y axes for drawing arcs sf = 100 'sets size factor CALL ispowerinit(10) 'sets power level (to 20%) speed% is speed in steps per second 'delay% = 2000000 / speed% 'calculates delay between steps for speed setting CALL issetspeed(32767) 'sets stepper motor speed to speed steps per second CALL issetmode(0) 'sets motion stage to relative mode PRINT "Starting Movement"

```
CALL drawSQ(sf)
```

```
INPUT "Return to Starting Position (1=yes, 0=no)? ", origin
CALL issetspeed(20000) 'sets speed to 100 steps/sec
IF origin = 1 THEN CALL ismover(0, 0, 0, 0, exitcode%)
END
```

```
SUB checkexit (exitcode%) 'Add parameter eoe% for End On Error option
IF NOT exitcode% = 0 THEN
SELECT CASE exitcode%
CASE exitcode% = 1 TO 2
PRINT "Limit Switch Encountered - M1"
CASE exitcode% = 3 TO 4
```

PRINT "Limit Switch Encountered - M2" CASE exitcode% = 5 TO 6**PRINT "Limit Switch Encountered - M3"** CASE exitcode% = 7 TO 8 PRINT "Limit Switch Encountered - M4" CASE exitcode% = 32PRINT "Encoder Error on M1" CASE exitcode% = 33PRINT "Encoder Error on M2" CASE exitcode% = 34PRINT "Encoder Error on M3" CASE exitcode% = 35 PRINT "Encoder Error on M4" CASE exitcode% = 51 **PRINT "Shield Open"** CASE exitcode% = 129 PRINT "Keyboard Abort (ESC)" CASE exitcode% = 185 PRINT "Keyboard Pause (spacebar)" CASE ELSE PRINT "Move Unsuccessful - Reason Unknown" **END SELECT** 'IF eee% = 1 THEN END **END IF END SUB**

SUB drawSQ (sf)

CALL issetspeed(2000000 / 1000) 'sets speed to 1000 steps/sec CALL ismover(0, 0, -365, 0, exitcode%) 'unblocks laser IF exitcode% THEN CALL checkexit(exitcode%) 'error check CALL issetspeed(32767) 'returns to writing speed

CALL ismover(8 * sf, 0, 0, 0, exitcode%) 'first leg IF exitcode THEN CALL checkexit(exitcode%) 'error check CALL ismover(0, 8 * sf, 0, 0, exitcode%) 'last leg IF exitcode THEN CALL checkexit(exitcode%) 'error check CALL ismover(-8 * sf, 0, 0, 0, exitcode%) 'first leg IF exitcode THEN CALL checkexit(exitcode%) 'error check CALL ismover(0, -8 * sf, 0, 0, exitcode%) 'last leg IF exitcode THEN CALL checkexit(exitcode%) 'last leg IF exitcode THEN CALL checkexit(exitcode%) 'last leg IF exitcode THEN CALL checkexit(exitcode%) 'error check

CALL issetspeed(2000) 'sets speed to 1000 steps/sec CALL ismover(0, 0, 365, 0, exitcode%) 'blocks laser IF exitcode THEN CALL checkexit(exitcode%) 'error check END SUB

APPENDIX F

Software program for the motion stage control, composed by the QuickBasic, Microsoft.

• Patterning for the circular contour track in Figure 96

```
DECLARE SUB draw1 (sf!)
```

```
DECLARE SUB checkexit (exitcode%)
DECLARE SUB drawO (sfl) 'draws the circle moving surface
'$INCLUDE: 'IS BC.BI' 'enables instep library
'$INCLUDE: 'QB.BI'
'Main Body
a = 1
b = 1
WHILE a = 1
CALL ischeckcard(592, checkcode%) 'checks to see if card is present
IF checkcode% = 0 THEN
       PRINT "Card not found."
        INPUT "Do you wish to try again (1=yes,0=no)"; b
ELSE a = 0
END IF
IF b = 0 THEN a = 0
WEND
IF b = 0 THEN END
CALL issetcardtype(1) 'sets the card type to QuickPhase half stepping mode
CALL issetcplane(1, 2) 'defines x and y axes for drawing arcs
                 'sets size factor
sf = 150
CALL ispowerinit(10) 'sets power level (to 20%)
speed% is speed in steps per second
'delay% = 2000000 / speed% 'calculates delay between steps for speed setting
CALL issetspeed(32767) 'sets stepper motor speed to speed steps per second
CALL issetmode(0)
                     'sets motion stage to relative mode
PRINT "Starting Movement"
CALL issetspeed(2000000 / 1000) 'sets speed to 1000 steps/sec
CALL ismover(0, 0, -365, 0, exitcode%)
                                         'unblocks laser
IF exitcode% THEN CALL checkexit(exitcode%) 'error check
CALL issetspeed(32767)
                              'returns to writing speed
INPUT "How many repetitions do you want?", x
FOR N = 1 TO x
        CALL draw1(sf)
NEXT N
CALL issetspeed(2000000 / 1000) 'sets speed to 1000 steps/sec
CALL ismover(0, 0, 365, 0, exitcode%)
                                         'blocks laser
IF exitcode THEN CALL checkexit(exitcode%) 'error check
```

IF origin = 1 THEN CALL ismover(0, 0, 0, 0, exitcode%) END SUB checkexit (exitcode%) 'Add parameter eoe% for End On Error option IF NOT exitcode% = 0 THEN SELECT CASE exitcode% CASE exitcode% = 1 TO 2 PRINT "Limit Switch Encountered - M1" CASE exitcode% = 3 TO 4 PRINT "Limit Switch Encountered - M2" CASE exitcode% = 5 TO 6 PRINT "Limit Switch Encountered - M3" CASE exitcode% = 7 TO 8 PRINT "Limit Switch Encountered - M4" CASE exitcode% = 32 PRINT "Encoder Error on M1" CASE exitcode% = 33 PRINT "Encoder Error on M2" CASE exitcode% = 34 PRINT "Encoder Error on M3" CASE exitcode% = 35PRINT "Encoder Error on M4" CASE exitcode% = 51 **PRINT "Shield Open"** CASE exitcode% = 129PRINT "Keyboard Abort (ESC)" CASE exitcode% = 185 PRINT "Keyboard Pause (spacebar)" CASE ELSE PRINT "Move Unsuccessful - Reason Unknown" END SELECT 'IF eoe% = 1 THEN END END IF **END SUB** SUB draw1 (sf!) CALL issetspeed(32767) 'returns to writing speed CALL ismover(0, -10.7 * sf, 0, 0, exitcode%) 'first leg IF exitcode THEN CALL checkexit(exitcode%) 'error check **END SUB**

INPUT "Return to Starting Position (1=yes, 0=no)? ", origin CALL issetspeed(20000) 'sets speed to 100 steps/sec

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