Femtosecond laser irradiation of synthetic single crystal diamond: studies of surface ripples and ablation thresholds

FEMTOSECOND LASER IRRADIATION OF SYNTHETIC SINGLE CRYSTAL DIAMOND: STUDIES OF SURFACE RIPPLES AND ABLATION THRESHOLDS

BY

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A THESIS

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Abstract

This thesis explores the ablation and texturing of synthetic single crystal diamond under ultrashort laser pulse irradiation in rough vacuum ambient conditions. The study has two main themes. First, the production of ordered periodic nanostructures, called ripples, on the diamond surface is characterized and the periodicity of these structures is analyzed against irradiation parameters. Second, the ablation thresholds for a wide range of numbers of incident ultrashort pulses on diamond is measured and the behaviour is analyzed. Experiments were performed with a 1 kHz repetition rate titanium sapphire laser system producing pulses at 800 nm central wavelength and 150 fs duration.

In the interpretation of many of these experiments, the issue of sample surface quality must be considered due to the presence of a thin layer of surface contamination and deep pitting (hundreds of nanometers) in the diamond surface. These factors are taken into account when discussing the results of the following studies. Future work with similar experiments performed on newly acquired, higher quality diamond samples is expected to mitigate these issues.

The study on ripples aims to provide a framework with which to test contesting theories of their formation and to attempt to control ordered sub-wavelength ripples formation. To this end, irradiation of single crystal diamond at a central wavelength of 800 nm was performed at normal incidence with a stationary beam ranging from a single pulse to 1000 pulses and fluences ranging from $\approx 26 \text{ J/cm}^2$ to below the damage threshold for each number of pulses. A train of ultrashort pulses was also scanned at low velocity across the polished diamond surface at fluences near the ablation threshold. The fundamental beam was frequency-doubled to a central wavelength of 400 nm and scanned across a polished surface at varying velocity near the ablation threshold. Irradiation was also performed at varying fluence and number of pulses for angles of incidence ranging from normal to grazing incidence $(0 - 85^{\circ})$.

The morphology and general outcomes are first summarized for each irradiation scheme, with unique or rare outcomes also highlighted. Ripples are usually found to fall into one of two categories, one with spatial period near the irradiation wavelength and one with spatial period near $\lambda/2n$, where λ is the central laser wavelength in air and n is the refractive index of diamond at λ . The former category is typically referred to as low spatial frequency laser induced periodic surface structures (low spatial frequency LIPSS, or LSFL). It is found that the rippled surface can vary in morphology between resembling sinusoidal behaviour, usually characteristic of LSFL, and having ordered, deep nanotrenches often characteristic of ripples having periodicity substantially below the irradiation wavelength. Ripples on diamond were found to be highly bifurcated and resisted the high order and coherence that might be desired for some industrial applications. By irradiation under complex schemes involving substantial material removal, grazing incidence interactions, and/or propagation through bulk diamond before interacting with a surface, striking ripples outcomes are reported with periodicities readily obtained below $\lambda/12$. A study of the dependence of ripples periodicity on the angle of incidence of ultrashort pulses leads one to conclude that the spatial period decreases with increasing angle of incidence for LSFL if the beam is p-polarized. A simple functional dependence is found, which is compared to theoretical predictions in the literature.

The second focus of this thesis is to investigate invisible accumulation of damage resulting from multiple ultrashort pulse irradiation leading to a reduction of the ablation threshold, a phenomenon referred to as incubation. To this end, ablation thresholds for single pulse up to 1000 pulse irradiation are determined using the D^2 method. The incubation behaviour is investigated by fitting to a power law model at both the fundamental central wavelength 800 nm and the second harmonic 400 nm. The power law model is used to provide a characteristic incubation coefficient, ξ (dimensionless), which describes the rate at which the ablation threshold is reduced.

The incubation properties are found to be sensitive to the incident laser wavelength. The single 800 nm pulse ablation threshold for synthetic single crystal diamond was determined to be 2.3 J/cm² with an incubation coefficient of 0.54. The single 400 nm pulse ablation threshold was determined to be 1.5 J/cm^2 with an incubation coefficient of 0.73. The measurements of these quantities are discussed as well as the applicability of incubation models.

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Chapter 1

Introduction

1.1 Motivation

In this thesis, ultrafast laser interactions with diamond are studied from two perspectives. First, the formation of periodic structures on surfaces due to irradiation is characterized and compared with models. Second, measurements of the ablation threshold are carried out to study the invisible accumulation of damage by multiple sub-threshold pulse irradiation, termed incubation.

Since the invention of the laser in 1960 by Theodore Maiman [1], researchers have developed a rich variety of laser types, which can be classified based on their emission properties. Rather than emitting a continuous beam of light, lasers can emit a series of pulses at a specified repetition rate. Various techniques were developed in order to achieve laser pulsing, including cavity quality factor switching (Q-switching), gain switching and cavity dumping [2]. These techniques can produce very short optical pulses down to several picoseconds (10^{-12} s) , but a more recent technique called modelocking can produce pulses as short as a few femtoseconds (10^{-15} s) . Modelocking was first demonstrated using an acousto-optic modulator inside a helium neon laser [3]. The modelocking phenomenon is described in detail in Section 2.1.1. When pulse durations are less than a few picoseconds, they are said to be in the ultrashort or ultrafast pulse regime. The present work is aimed at studies of laser beam interactions with transparent materials using ultrashort light pulses on the order of one hundred femtoseconds.

The invention of the laser also made very high optical energy densities available, which, combined with optical precision, led to the use of lasers in material modification, cutting and micromachining [4, 5]. The laser even became a primary precision cutting tool in some manufacturing plants [4].

With the ability to generate ultrashort optical pulses, the instantaneous power can reach substantially higher values than those achievable with longer pulses. For example, if we assume a Gaussian pulse shape, a 10 nanosecond (ns) pulse with 10 μ J of energy has a peak power of 2×10^3 W, while a 100 femtosecond (fs) pulse with the same energy has a peak power of 2×10^8 W. The increased peak power allows one to achieve higher intensities, which leads to a new outcome for the interaction of light with matter.

Long pulses (more than a few picoseconds) can deliver their energy to a transparent material primarily through surface states, bulk defects and quasi-free seed electrons, which need to gain sufficient energy to collisionally ionize neighbouring electrons to sustain the avalanche process [6]. This means that extremely high pulse energies are required for machining with long pulses since the majority of light is transmitted, with less transmission occurring as the pulse duration is decreased [7]. It also means that the absorption properties are probabilistic, with high uncertainty in the amount of seed electrons available for absorbing energy from each pulse. The uncertainty arises because transparent materials have very few free electrons and so a pulse may or may not interact with a sufficient number of them to heat the material to critical levels [6]. On the other hand, ultrashort laser pulses are intense enough to drive multiphoton ionization of a transparent material even with relatively low pulse energies. Following multiphoton absorption, free carrier absorption and avalanche ionization may occur [7, 8]. As a result, the energy is delivered much more efficiently. Moreover, the nature of absorption on femtosecond time scales means that all of the energy is absorbed before the lattice can draw heat away, meaning that the energy is deposited locally, in contrast to longer pulses which rely on thermal processes and result in substantial collateral damage. One such transparent material that has generated considerable interest in modern electronic and optical applications is diamond.

Diamond is an attractive material for both industry and fundamental research. It has a wide band gap (5.47 eV), is transparent to an extremely wide band of light frequencies (from UV to far IR), and has a high refractive index of 2.4 [9]. It is the hardest naturally occurring material, it has very high thermal conductivity and high resistance to thermal shock, and can even perform as a semiconductor with appropriate doping [10]. This makes it suitable for many optical applications. Diamond is highly resistant to conventional cutting and machining, as well as optical machining unless ultrashort pulses are used.

From a scientific and industrial standpoint, it is important that a material be accessible and have reliable properties. Recently, synthetic diamond has become increasingly available and is of exceptionally high quality [11]. Diamond can be manufactured with impurity concentrations down to 1 ppb or less and control of the growth process allows the properties of the material to be predictable.

Prior work, performed by former M.Sc. student from our research group Nicholas Mailman, provided a component of the motivation for this work [12]. His findings of nanostructures with diameters on the order of 100 nm sparked an interest because of potential applications in nanotechnology [12]. The first goal was to reproduce the experiments to investigate the morphology of these structures. The parameter space was also expanded in search of novel morphologies. Sharp nanostructures may have applications in field emission devices [13] as well as single photon emission for scientific purposes [14].

Historically, research into ripples formation has generated considerable interest because of their potential in the above applications, in addition to applications in microelectromechanical systems (MEMS) and optical gratings. The use of new materials such as diamond in these devices is still a growing field and, in the case of electronics, may offer niche advantages over silicon [10].

Nanostructuring with laser pulses can occur spontaneously for a broad range of irradiation conditions and the resulting structures are called ripples, due to the first observations of these structures, which had a wavelike structure [15]. The mechanisms for ripples formation are still not agreed upon despite considerable research effort [16–25], while ripples are a universal phenomenon appearing on nearly every material following irradiation [26, 27]. It is also likely that the important mechanisms for ultrafast laser processing are different from the mechanisms proposed for longer pulses or continuous wave irradiation [16, 23, 25]. This topic exemplifies the remaining challenges in understanding light-matter interaction.

Other motivations stemmed from our group's expertise in the characterization

of ablation thresholds in silicon and other semiconductors [28–30]. As the use of diamond in optical devices increases [31], a good understanding of the optical breakdown properties, which determine ablation thresholds, becomes increasingly relevant. Specifically, the invisible accumulation of damage due to sub-ablation threshold pulse irradiation, termed incubation, may be an important property to quantify for the use of diamond in high power applications (for example, as a Raman-shift material in neodymium lasers to produce a high power source in the yellow portion of the visible spectrum) [32]. Beyond that, the physical mechanisms behind incubation in dielectrics and semiconductors have not been conclusively identified, making the question interesting scientifically [33, 34]. Studying the effect on a variety of materials will aid in determining these mechanisms.

This thesis presents experimental findings of ultrashort pulse interactions with synthetic single crystal diamond. Findings of ripple formation for a variety of irradiation energies, pulse numbers, wavelengths and geometries are presented and discussed. Analysis of the periodicities and a description of the possible outcomes are given. Findings of the multiple pulse ablation properties are also presented in the context of incubation, described in detail in Section 1.2.5. The challenges associated with performing surface and bulk light-matter interaction experiments on synthetic single crystal diamond plates is also discussed. Subtle issues involving surface contamination and its possible origins, surface quality, polishing, manufacturer-defined roughness and its relationship to actual surface morphology, and sample point or extended defects having effects on absorption or birefringence are investigated.

1.2 Background

1.2.1 Interactions of ultrafast laser pulses with dielectrics

Transparent dielectrics typically do not absorb light because the incident photons have energies far below that of the material band gap. However, the higher intensities associated with ultrashort pulses can lead to nonlinear absorption processes [8, 35]. When the photon density reaches a critical level the probability of absorbing several photons simultaneously becomes significant. In addition, the high fields that result from high photon densities can distort the band structure of the material. As a result, electrons in the valence band can be promoted to the conduction band through multiphoton and tunnelling ionization [8, 35].

If the intensity is high enough, multi-photon and tunnelling processes may dominate the ionization of the target region. However, in most cases, impact ionization is proposed to play an important role in free carrier generation [7]. Impact ionization is initiated by free carrier absorption (FCA), in which free electrons in the presence of the attractive ions, which act as a momentum sink, absorb photons through inverse Bremsstrahlung [36]. If the collisional cross section between free and bound electrons is high enough, the free electrons will collisionally ionize atoms after sufficient energy has been absorbed. It is important that the pulse be very intense so that the rate at which free electrons absorb energy exceeds the rate the energy can be delivered to the lattice by electron-phonon coupling. Newly free electrons carry out this process repeatedly, causing avalanche breakdown.

The rates at which these processes occur are highly dynamic. The rates depend on the intensity of the laser pulse and the optical properties of the material, both of which vary significantly during the pulse. We can describe the time evolution of an ultrashort pulse exciting a dielectric surface qualitatively. The leading edge of a pulse with Gaussian temporal profile is transmitted. As the intensity increases, multi-photon processes take place leading to the generation of free carriers. These free carriers cause a change in the optical properties of the material. Some of the pulse is now reflected, while the energy that is not reflected is either transmitted or absorbed by multi-photon processes and free-carrier absorption. In addition to inverse Bremsstrahlung, free carriers may resonantly absorb incoming light if the carrier density is such that the plasma frequency equals the laser frequency, although this will only be the case in a transient manner. FCA leads to hot electrons with enough energy to collisionally ionize bound valence band electrons and avalanche ionization takes place. Multiphoton ionization continues as long as the intensity remains high enough. However, both multiphoton and avalanche processes saturate as the free carrier density reaches critical levels. One commonly postulated saturation point is the critical density (that is, the carrier density at which the plasma frequency equals the laser frequency) [7, 37]. The theory by Keldysh predicts that for high intensity and low frequency, multi-photon ionization will give way to tunnelling processes [35].

The propensity for tunnelling or multi-photon absorption processes to dominate is determined by the dimensionless Keldysh parameter,

$$\gamma = \frac{\omega}{e} \sqrt{\frac{mcn\epsilon_0 E_g}{I}},\tag{1.1}$$

where ω is the laser frequency, e is the electron charge, m is the electron-hole reduced mass, n is the refractive index, E_g is the band gap energy, and I is the laser intensity. If γ is much less than 1.5 then tunnelling ionization dominates, while for γ much higher than 1.5, multi-photon ionization dominates. Near $\gamma = 1.5$ both processes occur together. That is, a valence electron may absorb a number of photons with total energy less than the band gap and then tunnel to the conduction band [38].

Let us consider the case for a single near (slightly above) threshold pulse (intensity 1.5 TW/cm²) incident on a diamond surface with band gap 5.47 eV. In the absence of a good estimate of the electron-hole reduced effective mass, the free electron mass is used for an estimate. In this example, the Keldysh parameter is 2.7.

1.2.2 Rate equations for absorption of ultra short pulses in dielectrics

Numerous attempts have been made at simulating carrier excitation in dielectrics. One method is a straightforward single rate equation approach, which is well-suited to intensities for which multiphoton processes are dominant and requires little computing power. A simple numerical calculation of carrier densities at the surface of a dielectric are carried out here to illustrate the approach. Following [7, 8, 39], where the values for the constants may found, the rate of generation of carriers, \tilde{n} , is given by

$$\frac{d\tilde{n}}{dt} = \sigma^{(4)} \left(\frac{I(t)}{\hbar\omega}\right)^4 + \alpha(I(t),\tilde{n}) - \beta\tilde{n}^2.$$
(1.2)

To avoid confusion with parameters existing elsewhere in this thesis, the parameters are summarized here.

 \tilde{n} : carrier density

 $\sigma^{(k)}:$ k-photon multiphoton cross section

- I(t): laser intensity
- ω : laser frequency
- β : carrier recombination rate
- $\epsilon(\tilde{n})$: dielectric function
- $\langle e_e \rangle$: average free electron energy
- U: band gap energy
- m_e : mass of electron
- ν : electron collision frequency
- ϵ_0 : dielectric constant with zero free carriers

The first term is the multiphoton rate, written here for the case of four 1.55 eV photons being absorbed in diamond. The second term is the rate of avalanche ionization, which depends on the intensity and the number of available free carriers (or the dielectric function). The last term represents carrier recombination. The avalanche term given in [8] is

$$\alpha(I(t), \tilde{n}) = 2\frac{\omega}{c} \frac{\operatorname{Im}\{\sqrt{\epsilon(\tilde{n})}\}}{(\langle e_e \rangle + U)} I(t)$$
(1.3)

Using a Drude model to estimate the carrier density-dependent dielectric function can provide good results, as demonstrated in [8, 37]. This can be written as

$$\epsilon(\tilde{n}) = \epsilon_0 - \frac{\tilde{n}e^2}{m_e\varepsilon_0} \left(\frac{1}{\omega^2 + i\omega\nu}\right) \tag{1.4}$$

Combining these expressions and solving numerically with a Runge Kutta method can provide a guide to expected carrier densities reached during laser irradiation. For example, if we have a Gaussian pulse that is 170 fs in duration (FWHM), we get the carrier density shown in Figure 1.1.



Figure 1.1: Single rate equation simulation of electron density (blue curve) as a function of time for a 170 fs pulse (intensity shown in green) at 800 nm wavelength in diamond ($\epsilon_0=5.76$).

1.2.3 Material response following excitation by a single ultrashort pulse

Since the duration of the pulse is less than the electron-phonon coupling time, the lattice remains relatively cool during the absorption process, although it does begin to gain heat from the hot electrons. As the energy is transferred, several thermodynamic processes can occur, mostly involving rapid expansion and concomitant phase transitions. The lattice becomes fully thermalized after some picoseconds [7, 40, 41]. For fluences high enough to damage the target surface, melting and subsequent ablation occur. Melting can take place thermally over tens of picoseconds or non-thermally over just a few picoseconds. The extreme free carrier density caused by an ultrashort pulse may cause bond softening and homogeneous melt formation. This is in contrast to typical melting phenomenon in which nucleation occurs at an interface and a

melt front moves through the heated region. These phenomena were confirmed using time-resolved microscopy and reflectivity measurements [42].

This section deals with the material phase evolution following an excitation pulse with enough energy to cause ablation. In many cases, the initial state is one of a very hot electron gas and intact, cool solid lattice. However, it has been demonstrated that ultrafast melting can occur during the pulse, which will also be considered. Some of the deepest insights into the material response following ultrafast laser excitation has been provided by molecular dynamics simulations. These simulations have been compared against empirical results with some success. The predictions arising from these simulations are explained first, followed by select studies, which offer experimental support.

The molecular dynamics simulations in [43, 44] have identified four prominent ablation processes, distinguished chiefly by their thermodynamic trajectories. The four processes are spallation, phase explosion, fragmentation, and vapourization.

Spallation occurs for low fluences, just above the ablation threshold threshold. Ablation can occur directly through the solid phase for some materials if the energy is low enough (near threshold). When a light pulse hits a material, a fast pressure wave travels through and if the energy deposited is not great enough to soften the surface, the resulting pressure wave can cause the material to fail [43].

At slightly higher fluences, the target is heated isochorically, followed by a quasiadiabatic relaxation process. This process is called phase explosion or homogeneous nucleation. Since the material is heated too quickly to reach thermodynamic equilibrium, the relaxation is not entirely adiabatic. During the expansion, the phase changes proceed as follows: solid, solid/liquid, liquid, liquid/vapour (metastable).
Nucleation of gas bubbles occurs as a result of slight disturbances which lift the material from the metastable state, where it relaxes to a stable vapour state. These bubbles coalesce, causing ablation of large liquid droplets. The nucleation begins at approximately 20 ps, with fully formed liquid droplets noticeable before 100 ps [43]. This process involves the expansion of material which maintains a fairly sharp interface with the vacuum above and has been shown to be consistent with the Newton rings observed in pump-probe studies of material surfaces undergoing ablation [42].

With more energy, fragmentation becomes dominant. Heating is so intense that material becomes a superheated solid. That is, the heating happens too quickly for the material to respond with expansion. The superheated solid relaxes, melting first, then expanding as a super-critical (on the boundary of a phase transition) fluid. Voids form as a result of the strong gradient in heat causing a strong gradient in stress forces. Although similar to phase explosion, the fact that the gas phase exists before the condensed trajectory reaches metastable state (liquid/vapour) indicates that nucleation is not occurring. This process can be distinguished from phase explosion in that some of the material enters the vapour phase without passing through the metastable liquid/vapour phase [43].

A material may also absorb energy greater than its cohesive energy, resulting in decomposition into monomers. This process is called vapourization and the thermodynamic trajectories indicate that this is not a thermal process.

The timescales of all these processes (hundreds of picoseconds) are much longer than the duration of the pulse (less than one picosecond). The four processes above may occur simultaneously at different depths or lateral positions from the centre of the ablation site, resulting from the different amounts of energy absorbed. The above processes (with the exception of spallation) involve the deposition of sufficient energy into the material surface in order to induce rapid phase changes and ablation. Under low fluences, another process can dominate the ablation without depositing heat to the lattice. This process, called Coulomb explosion (CE), is characterized by the desorption of many monolayers of particles at high energy due to the removal of surface electrons leading causing the remaining charged ion cores to destabilize the lattice through Coulomb repulsion. Several reports have shown evidence that CE occurs for fluences near the ablation threshold up to a certain threshold, while the above processes dominate for higher fluences [45–48].

The discovery of this process was in part linked to the observation of strong and gentle ablation phases on dielectrics, and also in connection with incubation as the number of pulses increases [48]. Gentle ablation phase was marked by the removal of a few tens of nanometers per pulse, leaving behind a smooth or rippled surface with very little heat-affected-zone. In contrast, the strong ablation phase can be characterized by an order of magnitude higher ablation depth per pulse and complex, rough crater surface usually attributed to a phase explosion ablation process [45]. The abrupt transition between the two ablation phases and ejected ion analysis provided evidence for CE [46, 48]. Dielectrics undergo CE far more readily than semiconductors or metals because the latter two materials have excellent carrier transport properties, although CE is possible in these materials in some conditions [49, 50].

1.2.4 Periodic structures from irradiation with coherent sources

Laser-induced periodic surface structures (LIPSS, also referred to as ripples) have been observed on laser-processed materials since 1965 [51], and received a thorough theoretical description nearly 20 years later [26, 27]. However, a theoretical framework which fully describes the formation of ripples has not yet been established. In great part, this is due to the many different types of ripples and the many situations under which they can form. This section highlights significant theories behind LIPSS formation.

Low spatial frequency LIPSS (LSFL) are common in longer pulse lengths as well as ultrashort pulses. They often have a sinusoidal structure (at least approximately) and tend to have a periodicity on the order of the laser wavelength λ , or λ/n [15, 52].

High spatial frequency LIPSS (HSFL) are more common for higher numbers of pulses and seem to be unique to ultrashort laser pulses (i.e. they do not occur for nanosecond pulses) [21, 53]. Their morphology varies, in some cases resembling sinusoidal, while quite often having high aspect ratios or more bifurcations. HSFL tend to have a periodicity of at least a factor of two smaller than that of LSFL and are commonly found with a periodicity of $\lambda/2n$, where λ is the central laser wavelength in air and n is the refractive index of the material at λ [53]. In Figure 1.2, a comparison between LSFL and HSFL is shown.

A comprehensive theory relating the Fourier components of surface structures to the Fourier components of both incident light and light scattered by a rough surface was published in 1983 [26, 27]. The authors defined a quantity η called the efficacy factor, which is a function of wave vectors of scattered and incident light. The wave vectors corresponding to peaks represent the wave vectors of ripples on the surface for a given set of laser and material properties. Sipe et al. argue that a roughened layer on the surface with a depth much smaller than the laser wavelength causes scattering of the incident radiation into the bulk, where it interferes with incident radiation. The



Figure 1.2: Comparison between ripple periodicity and morphology for typical LSFL (left image) and HSFL (right image). Note that the left image does not accurately represent periodicity as a result of the sample being tilted by 50° for imaging. The ripple orientation is perpendicular to the incident polarization in both cases.

interference causes inhomogeneous energy deposition in the material. In contrast to past theories on ripple formation involving interference between scattered and incident radiation, Sipe theory does not invoke a standing wave description. Instead, local fields - resulting from radiation with longitudinal components of polarization - are accounted for and used as a correction to the transverse scattered wave. Therefore, their theory is not understood simply as standing wave interference. As the ripples begin to form the surface parameter changes, which enhances the formation of more ripples at the same frequency. The most common predicted relationship between ripple periodicity (Λ) and incident wavelength (λ) is

$$\Lambda = \frac{\lambda}{1 \pm \sin \theta}.\tag{1.5}$$

However, many other relationships can be predicted and have been experimentally

confirmed.

LSFL from femtosecond irradiation has been observed to have a periodicity slightly less than that of the incident radiation. This phenomenon was not observed at the time Sipe et. al. put forward their theory and was therefore not addressed. Recently, Huang et. al. [17] have addressed this by showing that the coupling between the incident radiation and surface plasmon polaritons is mediated by the existence of a surface grating. In addition, their invocation of surface plasmon polaritons has accounted for changes in the material properties due to laser-generation of free carriers (see equation (1.7), to follow). This coupling is claimed to affect the inhomogeneous energy deposition on the surface, causing the periodicity to decrease. Surface plasmons can be generated on metallic surfaces by light incident on a sub-wavelength aperture or other topological defect and it is plausible that surface roughness (due to existing surface imperfections or laser-induced) could initiate surface plasmon production on diamond. Although surface plasmons are forbidden in dielectrics, the action of ultrashort pulses causes transient carrier concentrations to rise to levels comparable with metals, allowing for a transient surface plasmon polariton propagation [17, 23]. We do notice the onset of periodic structuring in the vicinity of debris, even for single pulse irradiation, which makes surface plasmons at least plausibly connected to the formation of ripples. Huang et. al. predict a relationship between ripple periodicity and incident wavelength for p-polarized radiation that is

$$\Lambda = \frac{\lambda}{\frac{\lambda}{\lambda_s} \pm \sin \theta},\tag{1.6}$$

where

$$\lambda_s = \lambda \left(\frac{\epsilon' + \epsilon_d}{\epsilon' \epsilon_d}\right)^{1/2},\tag{1.7}$$

and θ is the incidence angle of the laser pulse. In equation (1.7), ϵ' is the real part of the dielectric constant of the excited surface and ϵ_d is the dielectric constant of the dielectric material at the sample surface (for our work in rough vacuum, $\epsilon_d \approx 1$). Notice that for $\theta = 0$ the ripple periodicity becomes

$$\Lambda = \lambda_s. \tag{1.8}$$

Going to the surface plasmon picture, we can offer some explanation of the general observations. Surface plasmon polariton wave vectors vary with charge densities and distributions, allowing a variation in observed periodic structuring periodicity depending on the local fluence and number of pulses. Furthermore, the existence of a grating on a surface can lead to a stop band for surface plasmon production. This could play a role in establishing the ripples dichotomy (LSFL and HSFL). The stop band occurs when the period of the surface grating is half that of the wavelength of the surface plasmon. This means that a region of surface plasmon frequencies are forbidden for certain surface grating periodicities. The SP frequency must be determined by the frequency of incident radiation, which means that there are a range of forbidden frequencies for a given grating periodicity or a range of forbidden grating periodicities for a given frequency.

Surface plasmons look like promising explanation given the sudden onset of periodic structuring in craters (even single shot) near a piece of debris or surface defect. There are groups which have observed surface plasmon initiation through the use of metal nanoparticles, bowties, and wire grids on a dielectric or semiconducting substrate [54, 55].

Although Sipe theory has been successful in predicting LSFL formation on surfaces, the theory as it was does not predict the formation of HSFL. In addition, the theory does not account for modified material properties such as free carrier excitation.

Other authors [21–23] argue that second harmonic generation (SHG) at a surface exhibiting LSFL leads to the production of HSFL. This conclusion is reached by observing the onset of HSFL after multiple pulse irradiation of InP. In particular, it is observed that HSFL begin to form when the LSFL have the strongest Fourier signal and the period is very nearly half that of the LSFL [22]. The theory arises from calculations of the efficacy factor which fail to mirror experimental results (HSFL periodicity).

This idea was developed further by Dufft et al. by studying LIPSS on ZnO and invoking the effects of free-carrier generation on the surface in addition to SHG at the surface[21]. To demonstrate SHG as a potential mechanism for HSFL formation, spectroscopic measurements were taken during irradiation of the ZnO surface with parameters which lead to HSFL creation. Scattered SHG light was observed with polarizations both parallel and perpendicular to the incident radiation; however, the latter was nearly three times more intense. A modified refractive index was calculated using the Drude model and considering the Kerr effect, the latter being deemed negligible. This modified refractive index and the second harmonic light were used as modified parameters in Sipe theory to calculate efficacy factors for comparison with experiment with some success. Particularly, an angle dependence was calculated and tested against experiment with remarkable agreement.

In their calculations Dufft et al. assumed 400 nm incident on the material, which is probably not exactly the case since it is produced somewhere in the material. In addition, the ripple period proved to be heavily dependent on free carrier density, which presents a problem because free carrier density is a dynamic variable and it is not known during the interaction while the ripples form. This problem was not addressed directly but reasonable estimates were made for the carrier density for each calculation.

In 2006, Bhardwaj et al. presented ripples results on fused silica along with an explanation involving the formation of plasma planes [24]. The periodic structures observed were more ridge-like than ripple like, similar to many observations of compound semiconductors and dielectrics [18, 53, 56, 57]. The pulse energy was insufficient to create the carrier densities required for a classical interference description of ripple formation to match observations.

The theory states that inhomogeneous deposition of energy resulting from any number of different processes (material defects etc.) leads to nanometer scale plasma spheres within the bulk of the material [24, 58]. Light then interacts with the spheres, being enhanced along the equator and suppressed at the poles, which leads to the development of a plasma plane. Light propagating through a material with many plasma planes will be restricted to modes similar to those allowed in a metal plane waveguide. The spacing of the plasma planes is established by ensuring that said modes are supported.

Enhancement factors have been calculated by solving Maxwell's equations at a boundary between a dielectric and material with dielectric constant $\epsilon = \epsilon_r + i\epsilon_i$. The enhancement factor for a metal and plasma differ as a result of the sign of ϵ_r , which is negative for a metal and between zero and one for an underdense plasma, which for low fluences is assumed to be the case. The negative dielectric constant allows for a resonance in the enhancement factors, while there is no such resonance for a small positive dielectric constant.

In a 1984 paper by G. T. Boyd, the enhancement factors for electric fields at a metal-dielectric boundary are provided [59]. He states that for a spherical surface, the shape-dependent part L_{LR} is equal to 3, which can be confirmed by the equations below. The enhancement factors for the parallel and perpendicular components of the electric field at a spherical or ellipsoidal boundary are

$$L^{in}_{\parallel} = L^{in}_{\perp} = L^{out}_{\parallel} = \frac{\epsilon_r}{\epsilon_d} L^{out}_{\perp}, \qquad (1.9)$$

where ϵ_r and ϵ_d are the real part of the plasma dielectric constant and the dielectric constant of the surrounding material, respectively, and

$$L_{\parallel}^{out} = L_{LR}L_p(\omega). \tag{1.10}$$

 L_{LR} depends on the shape of the ellipsoid, namely the semi-major and semi-minor axes (a and b, respectively) according to

$$L_{LR} = 1 - \frac{xQ_1'(x)}{Q_1(x)},\tag{1.11}$$

where

$$Q_1(x) = \frac{x}{2} ln\left(\frac{1+x}{1-x}\right) - 1$$
 (1.12)

is the Legendre function of the second kind,

$$Q_1'(x) = \frac{1}{2} ln\left(\frac{1+x}{1-x}\right) + \frac{x}{1-x^2}$$
(1.13)

is its first derivative, and

$$x = \frac{1}{\sqrt{1 - \left(\frac{b}{a}\right)^2}}\tag{1.14}$$

is the shape-dependent parameter.

The local plasmon enhancement factor, $L_p(\omega)$, is also somewhat shape dependent. It is also complex so the $L_p(\omega)$ appearing in the second equation (above) is the norm of the complex quantity. This factor has a resonance for dielectric constants < 0 but none for positive dielectric constants as in the case of an underdense plasma. These equations combine for a reasonably constant enhancement factor for any ellipsoid.

The enhancement of the fields around a nanoplasma can be described roughly in terms of dipole oscillations. If the nanoplasma is underdense the natural frequency at which a plasma oscillates (plasma frequency) is slower than that of the light field, just like an over-driven damped harmonic oscillator. It is easily shown that the electrons oscillate out of phase with the incident light for the right conditions. This interference phenomenon means that the boundary conditions alone (with little effect from shape) contribute to the field enhancement.

To determine spacing, the plasma nanoplanes are considered similar to stacked metallic waveguides. By matching the allowed modes with the enhancement by boundary conditions, it is determined that the spacing should approach $\frac{\lambda}{2}$. In diamond, this is 166 nm for 800 nm light but a range of values from 120-200 nm are typically observed [12, 18, 25]. Also, according to the Drude model for the dielectric function, the real refractive index decreases with increasing carrier density.

In addition to the coherent models, which are based on inhomogeneous energy deposition, models based on self organization have gained substantial support [16, 20, 46, 60–62]. The theory was first developed to explain self-organized nanostructuring of surfaces following ion beam sputtering [63] and self-organization of thin liquid films. The theory was applied to laser nanostructuring in light of similarities between outcomes of nanostructured surfaces from laser and ion beam sputtering. The best phenomenological description offered in the ripples manuscripts is that competition between surface erosion and smoothing leads to self-organization of a highly unstable thin molten layer on the material surface [64]. Self assembly models have had success predicting the morphology of ripples outcomes, especially for cases involving highly complex features caused by irradiation at high fluences. Quantitatively, the link between incident polarization and ripple orientation has been made by addressing the kinetic energy of electrons excited by the laser pulse. The equations for the surface morphology depend on how the energy is deposited, which is done directly by excited electrons. By accounting for the mean free path, which has directionality due to laser polarization, an asymmetric energy deposition occurs leading to the preferred orientation of the ripples [65]. Predicting periodicity has been a challenge for the selfassembly models. There have been no attempts to provide nominal values for ripple periodicity outcomes, although some dependencies are predicted. The periodicity according to these models should depend on the depth of energy absorption and the temperature of the surface, and the ripples dichotomy is addressed by noting that a frequency-doubling effect is routinely observed in other cases of self-assembly such as large bodies of water, or desert sand ripples [65].

1.2.5 Incubation

The single pulse ablation threshold has long been known to decrease as a function of increasing numbers of prior pulses to the same spot [66], although the mechanisms governing the behaviour of this decrease are not yet fully understood. The accumulation of damage (or simply memory of past pulses, since a specific form of damage has not been identified) is invisible. It seems to occur for any material, from metals to semiconductors to wide-band gap dielectrics. The earliest models predicted a power law dependence for the ablation threshold fluence of the N^{th} pulse, $\phi(N)$, according to an empirically determined incubation factor, ξ

$$\phi(N) = \phi_0 N^{\xi - 1},\tag{1.15}$$

where ξ is a dimensionless number less than one, with a lower incubation coefficient indicating stronger incubation behaviour. The above model was developed for accumulated stress in metals, with slip deformations building up under the surface initiated by shock waves or thermal stress from the sub-threshold laser pulses [66]. Although it matches reasonably with experimental data, it is unclear how this translates to the case of semiconductors and other crystals, which have very different material properties from metals. Some authors [33] suggested an exponential decrease in the ablation threshold, which would be indicative of the buildup of defect states within a crystal. A similar invocation of an incubation parameter, k and accounting for a threshold cutoff (a fluence below which ablation is impossible even for an infinite number of pulses, ϕ_{∞}) leads to a model for dielectrics and semiconductors,

$$\phi(N) = [\phi_0 - \phi_\infty] e^{k(1-N)} + \phi_\infty.$$
(1.16)

Ashkenasi et. al. had some success fitting their model with experimental data, especially for the first few laser pulses. It also accounts for the fact that weak laser pulses will not be able to cause damage even if an infinite number of them are incident on the surface. Support for this model was also lent by a group that performed incubation analysis on TeO₂ [67].

Chapter 2

Materials and Methods

2.1 Laser system

Femtosecond laser pulses are generated in a modelocking resonator and amplified using the chirped pulse amplification method. This laser system consists of a mode locked titanium sapphire (Ti:Sapphire) oscillator, a frequency-doubled neodymium vanadate (Nd:VO₄) continuous wave laser, a frequency doubled and Q-switched neodymium yttrium lithium fluoride (Nd:YLF) laser and a chirped pulse amplifier. The two neodymium solid state lasers are pumped by fibre-coupled diode stacks operating at a wavelength of 808 nm. A schematic of the laser system including output parameters is shown in Figure 2.1. The diode array is housed in a separate box to facilitate better cooling and to allow diode stacks to be replaced without realigning the cavity of each of the neodymium lasers. Laser diodes emit light which diverges asymmetrically. Fibre coupling is made possible by the use of a cylindrical lens at the diode array to capture fast-axis light emission.



Figure 2.1: Schematic of the chirped pulse amplified laser system.

Modelocking in the Ti:Sapphire oscillator is initiated by an acousto-optic modulator crystal and sustained by Kerr lens mode locking, producing 120 fs pulses with 10 nJ of energy at a repetition rate of 82 MHz. The principles of modelocking are as follows. A laser cavity can support radiation wavelengths that are half-integer divisions of the cavity length. A cavity supporting a wide bandwidth of frequencies (a range of 10 - 15 nm) in discrete modes emits modelocked pulses when all modes constructively interfere at one place within the cavity (see section 2.1.1). A good analogy is that of a Dirac-delta function approximated by a partial series of sine or cosine functions. Inside the chirped pulse amplifier, pulses are stretched to 220 ps using a diffraction grating to separate the bandwidth and reflective elements aligned to produce a wavelength-dependent beam path, creating an effective group velocity dispersion (GVD). Figure 2.2 shows a schematic of the pulse stretching process. One feature not shown in the diagram of the stretcher is a curved mirror, which reverses the direction of the GVD. A Pockels cell and thin film polarizer combination selects stretched pulses at a repetition rate of 1 kHz, directing them to a laser cavity containing a titanium sapphire crystal, which is pumped by 150 ns pulses at wavelength of 532 nm with 4 mJ of energy. The pulses make many round trips inside the cavity until maximal amplification is achieved and is switched out by a second Pockels cell and a thin film polarizer.



Figure 2.2: Simplified view of the stretcher. Note that only one diffraction grating is used in the Spitfire stretcher. The second diffraction grating here is used to simplify the geometry.

2.1.1 Generation of ultrashort laser pulses

Ultrashort pulse generation with full width at half maximum (FWHM) duration 120 femtoseconds is accomplished by modelocking. Modelocking is a phenomenon that occurs inside a laser cavity in which the cavity modes are locked in phase so that the electric field of each mode constructively interferes at a single point in time and space to produce a single pulse oscillating inside the cavity. A graphical representation of the alignment of ten modes modes is illustrated in Figure 2.3. In a laser cavity containing 14 nm of bandwidth there are approximately 40000 supported modes.



Figure 2.3: Contrast between the outputs of two lasers: one in which the cavity modes are locked in phase and another with modes having random phases. Note that the output, shown in black, is the squared sum of the modes shown in colour to depict intensity rather than electric field strength.

In order for a laser system to support modelocking, it must be developed to support a large bandwidth inside its cavity. Therefore, a gain medium with a broad

gain curve is required, along with mirrors which are highly reflective for a large bandwidth. To achieve modelocking, an intra-cavity element must introduce loss to the modes which do not contribute to modelocking, while minimizing loss for the modes which are locked in phase. Any modulation of the loss at a frequency equal to the round-trip frequency of the cavity will be able to achieve such an effect since pulsed lasing will experience less loss than continuous wave lasing. The phase of the modulation also plays an important role, so the modulating element must be phaseadjustable. In titanium sapphire laser systems modelocking can be sustained without the use of any active elements because of Kerr lensing within the gain crystal. Kerr lensing is a phenomenon in which a beam is focused in a medium with a nonlinear intensity-dependent refractive index. In such a medium, the refractive index of a Gaussian spatial mode is highest in the centre and falls off towards the edges, which causes the effective path length of the beam to be higher in the centre, which is equivalent to how a convex lens works. The focusing power for the Kerr lensing of a pulsed beam will be many orders of magnitude greater than for a continuous wave beam because the change in refractive index, which is linked to the focusing power, is intensity-dependent. Another nonlinear effect caused by the high intensities in the gain medium is self phase modulation (SPM). This can lead to dispersion in the modes, which brings them out of phase and lengthens the pulse duration. To counter this effect, glass prisms are placed in the cavity to introduce regular (linear) dispersion. Nonlinear interactions are avoided in the prisms due to the different nonlinear properties of the material as well as the larger beam radius. These serve a dual purpose in combination with a slit placed between two sets of prisms. The slit selects the desired wavelengths of light since they are spatially separated due to dispersion.

The loss modulating element in the laser system used here is an acousto-opic modulator. This is a transparent crystal connected to a piezoelectric oscillator driven by a radio frequency pulse. The mechanical oscillations in the crystal cause Bragg scattering of the cavity modes, which means the scattering angle depends on the wavelength of sound in the crystal. Therefore, the crystal material must be chosen to introduce the correct amount of scatter.

In Kerr lensing the nonlinear refractive index is given by

$$n = n_0 + I n_2, \tag{2.1}$$

where n_0 is the refractive index of the medium, and n_2 is the (second order) nonlinear refractive index of the material. The critical power to initiate self-focusing is given in [68]

$$P_{cr} = \alpha \frac{\lambda^2}{4\pi n_0 n_2},\tag{2.2}$$

where α is a constant that depends on the beam profile, and λ is the wavelength of light in vacuum. Therefore, the placement of a slit in the cavity or using a narrow pump beam will lead to greater loss for the wider continuous modes than those which are locked.

2.1.2 Micromachining system

Laser micromachining control is described in this section. The beam is directed with highly reflective multi-layered broadband dielectric mirrors, with a wavelength range of 700 nm to 900 nm. A telescope shrinks the beam radius from 6 mm to 4 mm to allow clearance through smaller aperture optics without clipping. This is important for maintaining beam quality at the sample after the focusing optic by avoiding detrimental diffraction effects. For experiments requiring subtle modification or gentle texturing (at average powers of 60 mW or less), a 20% beam splitter is placed before the telescope and other pulse-manipulating optics. This pulse-energy reduction is intended to reduce nonlinear effects that may result from a smaller beam radius with high pulse energy (when high pulse energy is not required).

Fine control of the pulse energy is carried out by a set of thin film polarizers and half-wave plates (one under computer control). Older experiments achieved pulse energy control with the use of an initial half-wave plate and polarizer combination and computer-controlled reflective neutral density filters to automate the final pulse energy. In both setups, the initial thin film polarizer reduces the magnitude of prepulses, although these pulses do have components in both the x and y direction, so they cannot be completely eliminated. Thin film polarizers rely on high reflective coatings and being oriented at the Brewster angle to separate the s- and p-polarized components of an incident beam. There are two half-wave plates and three thin film polarizers alternating. The first half-wave plate is manually controlled to tune the maximum power while the second is computer controlled for continuous, automated power adjustment.

If experiments are to be done with 400 nm pulses, a frequency doubling β -barium borate (BBO) crystal is placed before the second wave plate. A Glan type cube polarizer is placed after the energy control to ensure polarization purity. The beam is aligned through the final focusing optic using a charge coupled device (CCD) for higher precision than that offered by a detector card. An example of a CCD captured beam profile is shown in Figure 2.4. Such images were recorded for each experimental run to monitor beam quality. Focusing was performed by a variety of optics from near diffraction-limited objectives to long focal length planoconvex lenses.



Figure 2.4: CCD image of beam profile (top left corner) and intensity cross sections along two axes (right). This beam profile was measured for the beam to be used in experiments on ripples presented in Section 3.1.1 and experiments on incubation summarized in Figure 3.41.

The sample is situated in a four inch diameter stainless steel vacuum chamber with a two inch interchangeable window opening. A one or two inch window is used where appropriate. The window must be chosen to have minimal thickness to avoid dispersive and nonlinear effects, while also maintaining enough rigidity to avoid deformation caused by the rough vacuum. The chamber accepts buffer gases through an additional port with shutoff and needle valve control.



Figure 2.5: Overview of micromachining system. The beam travels right to left through polarizer and half wave plate combinations (only one shown). The chopper is optional and used to lower the repetition rate.

2.2 Pulse diagnostics

Pulse duration is routinely measured with a noncollinear intensity autocorrelator. An autocorrelator is a device that uses the pulse to measure its own temporal shape. It should be noted, however, that detailed pulse profiles cannot be obtained in this way. Mathematically, the intensity autocorrelation function is the convolution of an intensity profile with itself.

$$A(\tau) = \int_{-\infty}^{+\infty} I(t)I(t-\tau)dt$$
(2.3)

This is achieved in the laboratory by splitting a pulse in two with a beam splitter and causing each of the resulting pulses to pass through each other along different beam paths in a non-linear optical crystal. When the pulses overlap, a signal is produced which is then measured by a photodetector and recorded. A time delay is introduced to one of the pulses, which allows one to use the strength of the signal and time delay together to measure the duration of the original pulse. A diagram showing this system is shown in Figure 2.6. Note that three signals are emitted from the nonlinear crystal. This is a result of the superposition of the electric fields of the two overlapping pulses driving second harmonic generation in the forward direction. Also, an additional window is placed in one arm of the interferometer (the arm for which the pulses are reflected from the beam splitter) to introduce dispersion equal to the dispersion introduced by transmitting through the beam splitter.

Temporal pulse characteristics are periodically characterized using a GRENOUI-LLE (Grating-Eliminated No nonsense Observation of Ultrafast Incident Laser Light E-fields) to ensure optimal pulse conditions, such as the absence of pulse front tilt or spatial chirp. A GRENOUILLE operates similarly to an autocorrelator in that pulses are used to measure themselves. The device folds a pulse in on itself using a Fresnel biprism just as it passes through a thick frequency doubling crystal (see Figure 2.7). The thick crystal causes different spectral components to separate in the vertical direction, while the time information is mapped to the horizontal spatial direction. This allows information about the phase to be obtained, as well as the spectrum and pulse duration. Furthermore, pulse front tilt can be detected as a horizontal shift of the trace.



Figure 2.6: Noncollinear autocorrelator setup showing the iris (D), beam splitter (BS), two retro-mirrors (R1 and R2), directing mirror (M1), focusing lens (L), non-linear barium borate crystal (BBO) for second harmonic generation, and photodetector. The delay is accomplished through use of a computer-controlled motorized stage.



Figure 2.7: Schematic of GRENOUILLE showing the cylindrical lens (C1), Fresnel biprism (FB), thick second harmonic generating crystal (SHC) and final collimating lens system (C2). The output from SHC is spectrally resolved because of narrow phase-matching bandwidth allowed by the thick crystal, which is very sensitive to the difference between propagation angle and the optical axis of the crystal.

2.3 Irradiation conditions

2.3.1 Normal incidence stationary irradiation

Experiments were performed by irradiating a polished diamond surface at normal incidence to study incubation and ripples behaviours. Some experiments were performed at a wavelength of 400 nm, using a 500 μ m thick beta barium borate (BBO) crystal in the beam path. Beam quality is not expected to be adversely affected by this conversion, as a result of the thin crystal [69]. Four broadband dielectric mirrors coated for high reflectivity at 400 nm were used to direct the beam to the focusing optic and dump unconverted light at 800 nm. The beam was focused using a 5× objective (approximate $1/e^2$ spot size of 5 μ m) for 800 nm work, while focusing with a 125 mm lens (approximate $1/e^2$ spot size of 11 μ m at $\lambda = 400$ nm) was used in addition to the 5× objective for 400 nm work.

2.3.2 Scanning surface irradiation

Stepper motors move samples in two dimensions with micrometer precision. The effective number of shots is calculated by adding the total energy incident on the surface from all pulses moving over a single point. The beam is assumed to have a Gaussian spatial profile. We can write an equation for the sum of the energy, normalized according to the Gaussian energy distribution (equation (2.4)). This quantity represents the effective number of pulses incident on the surface.

$$N_{\text{eff}} = \sum_{k=-\infty}^{\infty} e^{-\frac{2(x-k\nu/f)^2}{\omega^2}}$$
(2.4)

Where in equation (2.4) we have defined v as the scan velocity, f as the laser repetition frequency, and ω as the $1/e^2$ spot size. We then notice that multiplying this sum by v/f gives a Riemann sum, which, for $v/f \ll 1$ can be approximated by the integral

$$\sum_{k=-\infty}^{\infty} e^{-\frac{2(x-kv/f)^2}{\omega^2}} \left(\frac{v}{f}\right) \approx \int_{-\infty}^{\infty} e^{-\frac{2x^2}{\omega^2}} dx$$
(2.5)

$$=\sqrt{\frac{\pi}{2}}\omega,\qquad(2.6)$$

where we have used the Gaussian integral identity for equation (2.6). Finally, noting that the left hand side of equation (2.5) is equal to $N_{\text{eff}}(v/f)$, we get

$$N_{\rm eff} \approx \sqrt{\frac{\pi}{2}} \frac{f\omega}{v} \tag{2.7}$$

2.3.3 Surface irradiation at varying angles of incidence

Polished synthetic diamond samples were irradiated at varying angles of incidence to investigate the effect on ripples formation. Samples were mounted on a scanning electron microscope stub, held at the chosen angle by a manually controlled rotation stage, drilled to accept the SEM stub. Zero degrees incidence was calibrated using a standard hand level with the stub mounted on the stage, with the assembly held by a post-holder on the optical table.

2.3.4 Bulk and rough side edge irradiation

Laser processing of the rough side edge and bulk diamond is illustrated by Figure 2.8. The beam was focused with a 50× objective (focuses to an approximate 2.5 μ m beam waist in rough vacuum) 100-200 μ m below the diamond surface. Due to nonlinear effects in the bulk diamond, it is expected that the focusing conditions will vary from the predictions of linear optics. The focal point is scanned at constant velocity and depth (parallel to the surface), exiting the rough side edge of the sample. The scan speeds used were 1 μ m/s, 5 μ m/s, 10 μ m/s, and 50 μ m/s. Material processing on the rough side edge was investigated using electron microscopy techniques.



Figure 2.8: Irradiation geometry for irradiation of rough side edge.

2.3.5 The D^2 method

Physicists and engineers may be interested in the threshold for the ablation or damage or other optically-induced change on a material's surface. The D^2 method determines this threshold and provides information about the beam shape and size as it strikes the surface. Consider a beam with a Gaussian spatial distribution. The fluence, ϕ is distributed as

$$\phi(x,y) = \phi_0 e^{-2\left(\frac{x^2}{\omega x^2} + \frac{y^2}{\omega y^2}\right)},$$

which we can write as

$$\phi(x,y) = \phi_x(x) \cdot \phi_y(y) = \phi_{0x} e^{-2\frac{x^2}{\omega_x^2}} \cdot \phi_{0y} e^{-2\frac{y^2}{\omega_y^2}}.$$

We can write this in terms of the diameter, by substituting $\frac{D_{x(y)}}{2}$ for x(y). With this substitution we have

$$\phi_x(D_x) \cdot \phi_y(D_y) = \phi_{0x} e^{-\frac{D_x^2}{2\omega_x^2}} \cdot \phi_{0y} e^{-\frac{D_y^2}{2\omega_y^2}},$$

which leads to

$$\ln \phi_x(D_x) + \ln \phi_y(D_y) = \ln \phi_{0x} - \frac{D_x^2}{2\omega_x^2} + \ln \phi_{0y} - \frac{D_y^2}{2\omega_y^2}$$
(2.8)

$$\ln \phi_x(D_x) - \ln \phi_{0x} + \frac{D_x^2}{2\omega_x^2} = \ln \phi_{0y} - \ln \phi_y(D_y) - \frac{D_y^2}{2\omega_y^2} = K$$
(2.9)

We can arbitrarily assign K = 0 and justify it later.

$$D_x^2 = 2\omega_x^2 \left(\ln \phi_x(D_x) - \ln \phi_{0_x} \right)$$
(2.10)

$$D_y^2 = 2\omega_y^2 \left(\ln \phi_y(D_y) - \ln \phi_{0y} \right)$$
(2.11)

Furthermore, we can recognize that ϕ_{0x} and ϕ_{0y} are the fluences at which D_x and D_y tend to zero, respectively. Our assumption that the damage threshold is completely deterministic means that for a given measurement of a crater $\phi_x(D_x) = \phi_y(D_y) = \phi_{th}$. Therefore, setting the left side of equations (2.10) and (2.11) to zero yields $\phi_x(0) =$ $\phi_y(0) = \phi_{0_x} = \phi_{0_y}$. To sum up, we have

$$\phi_{0x} = \phi_{0y} = \phi_0 \tag{2.12}$$

$$\phi_x(D_x) = \phi_y(D_y) = \phi(D), \qquad (2.13)$$

where we have defined the variables ϕ_0 and $\phi(D)$ for brevity. Therefore we can conclude

$$\frac{D_x}{\omega_x} = \frac{D_y}{\omega_y} \tag{2.14}$$

We can now define D and ω as the geometric means of the diameters and spot sizes, respectively, where $D = \sqrt{D_x D_y}$ and $\omega = \sqrt{\omega_x \omega_y}$. Using this definition, along with (2.14), we get

$$\frac{D_x^2}{\omega_x^2} = \frac{D_y^2}{\omega_y^2} = \frac{D_x D_y}{\omega_x \omega_y} = \frac{D^2}{\omega^2}$$
(2.15)

Substituting (2.12) - (2.15) into equation (2.8) gives

$$D^{2} = 2\omega^{2} \left[\ln \phi_{0} - \ln \phi(D) \right]$$
(2.16)

Finally, we note that $\phi_0 = 2E_0/(\pi\omega^2)$, where E_p is the pulse energy and $\phi(D) = 2E_{th}/(\pi\omega^2)$, where E_{th} is the threshold pulse energy for a beam with radius ω . This gives a fitting equation.

$$D^2 = 2\omega^2 \left[\ln E_p - \ln E_{th}\right] \tag{2.17}$$

2.4 Material quality and selection considerations

Singe crystal diamond samples grown by chemical vapour deposition (CVD) were obtained from Element Six Ltd. Experiments were performed on type IIa single crystal diamond plates. The plates had dimensions of either $3.0 \times 3.0 \times 0.3$ mm (later samples used for surface experiments) or $3.0 \times 3.0 \times 0.5$ mm (earlier samples used in bulk modification experiments) and were polished to optical smoothness prior to exposure to intense radiation. Each plate was either polished on two sides (P2) or one side (PL). The mean roughness parameter (R_a) for each type of polishing is < 30 nm for P2 and < 10 nm for PL diamond. Type IIa diamond is very low in nitrogen impurities, containing less than 1 ppm of nitrogen in our samples, which reduces linear optical absorption to negligible amounts (< 1 cm⁻¹). Diamond specimens were oriented with the polished face in the $\langle 100 \rangle$ direction.

2.4.1 Sample quality issues

The roughness parameter is calculated by $\frac{1}{N} \sum_{i=1}^{N} (y_i - \bar{y})$, where y_i is the height of point i, \bar{y} is the average height of the surface, and N is the number of points for which R_a is calculated. It should be noted that the mean roughness value does not indicate the depth of valleys or peaks on the sample, but an average over the surface. The sample consisted of deep pits on the order of 100 nm or more with extremely smooth surface ($R_a < 1 \text{ nm}$) in between. This was verified by atomic force microscopy (AFM) analysis performed by an Element Six research scientist as well as AFM analysis performed at the Canadian Centre for Electron Microscopy (CCEM) and is shown in Figure 2.9.

The pitting can be problematic when attempting to determine ablation thresholds.



Figure 2.9: AFM surface map of pristine single crystal diamond plate polished to a mean roughness parameter $R_a = 5$ nm.

Sharp surface irregularities can lead to the well-known localized field enhancement effect at sharp structures at an interface [70]. Therefore, the spacing (several microns) of the pits may cause inconsistencies in the threshold measurements, especially for small spot sizes.

When diamond is grown by CVD, lattice dislocations can accumulate in the material as it is grown, which can have an effect on the refractive index as a result of the strain induced on the lattice. This strain induces a birefringence with a wandering slow axis direction, due to the random location of the extended defects. The birefringence $(n_o - n_e)$ is typically less than 10^{-4} [11].

Further to the issues of pitting, the samples can develop a thin surface layer of contamination, which appears to be dark and carbonaceous. Its origin is not certain and may be caused by the following factors: heavy processing of the material leading to a re-deposition of ablated material, sample mishandling and contamination from contact with surfaces, or contamination from vacuum systems (e.g. during scanning electron microscopy). In addition to the deposition of laser-ablated debris, heavy material processing can cause heating of the surface, which could lead to the conversion of a near-surface region to graphitic carbon, a well-documented effect of heated diamond, due to its inherently unstable crystalline state. Temperatures need to be raised to approximately 1000 K [71] (very far from the irradiation site) for this to happen and it appears from straightforward calculation that this latter possibility should not be achievable with the irradiation conditions used here. In contrast, the debris from ablation can easily reach any point on the sample surface.

2.4.2 Attempts to remove surface film

Surface contamination has been observed on several single crystal diamond samples obtained from Element Six Ltd.. According to a representative from Element Six, diamond surfaces readily pick up contaminants. The origin of contamination is not known with certainty, although several plausible contributors come to mind.

For one, the diamond samples were cleaned between experimental runs in baths of acetone, methanol, and de-ionized water. Of the three, contamination is most likely to arise from acetone since it does not have the same levels of purity as can be found in water or methanol and it picks up contaminants from the air and surfaces very easily. Other potential causes include the deposition of ablated material and picking up grime from surfaces (if placed face down, for example). The contamination was not detected on all samples. The film was also not uniform across the entire sample, although substantial portions of one sample appeared to contain a nearly uniform film. There appeared to be a concentration of contamination near ablation craters, although it is not necessary that the film produced near ablation craters is related to the film found elsewhere on the sample.

The composition of the surface layer is also in question. It could be deposited amorphous carbon, similar to graphite, or diamond-like-carbon but could also contain hydrocarbons and other substances. The composition is challenging to analyze because it is so thin. Our best estimate for the thickness is in the range of tens of nanometers to a hundred nanometers, depending on the location on the sample. This meant that X-ray analysis using the electron microscope was unable to distinguish the surface layer from the underlaying diamond. The matter was not pursued further.

A laser based method for removing the surface film was implemented after basic cleaning failed. Plasma cleaning was also performed, which successfully removed surface contamination. However, the surface appeared more heterogeneous under optical and scanning electron microscopy, which raised concern about the integrity of the surface. Therefore, a laser-based technique as attempted to remove the film thermally using nanosecond pulses while leaving the underlying diamond surface unharmed (by choosing nanosecond pulse energies that were presumably below the diamond damage threshold). Since the sublimation and boiling temperatures of diamond and amorphous carbon are so similar, we planned to take advantage of different absorption characteristics to ensure that diamond remained unheated. Graphite has an absorption coefficient of $11.5 \ \mu m^{-1}$ at 800 nm, while diamond has an absorption coefficient of effectively zero.

Unfortunately, the thermal diffusion coefficient for graphite parallel to the plane direction is $122 \text{ cm}^2/\text{s}$, ten times that of diamond. Over 6 ns, the diffusion length is

17 μ m (note: this number does not quite apply since it assumes a constant boundary temperature but it does give an idea for how spread out the energy becomes). Heat is not readily transferred perpendicular to the graphite planes, with a diffusion coefficient of only 0.036 cm²/s. This made nanosecond pulses inefficient choices for heating graphite to appropriate temperatures.

A Spectra Physics Spitfire LCX regenerative amplifier was set up as a nanosecond laser by placing a vertical retro-mirror immediately before the compressor and allowing the amplifier cavity to lase without seeding from the stretcher (see section 2.1 for diagrams and system overview). This system was pumped by the Evolution with 4 W average power of light at 532 nm wavelength and a repetition rate of 1 kHz.

The output was a 1 kHz train of 799 nm 6.56 ns pulses, as measured using a fast photodiode and 250 MHz oscilloscope. The power was controlled using neutral density filters with initial powers of 1 and 10 mW using a half-wave plate and thin film polarizer combination. Neutral density filters with an optical density (O.D.) of X attenuated the beam further by a factor of 10^{-X} . A 125 mm lens ($1/e^2$ spot size $\approx 20 \ \mu$ m) was used for focusing. At 1 mW, 500 μ m lines were written at 500 μ m/s with decreasing energy. Since no changes were observed, the experiment was repeated over the same area at 10 mW (Figure 2.10). In addition, the power was set to 10 mW and 15 lines 200 μ m long were cut at 50 μ m/s (Figure 2.10). A patch was also cut at full power and at 500 μ m/s with 40 μ m spacing between lines (Figure 2.10).

The results indicate that the surface layer can be removed with energetic nanosecond pulses at 800 nm but not without causing some damage to the diamond surface. In addition, damage was observed optically within the bulk of the diamond.

The results for 500 μ m/s are slightly skewed due to the surface being pre-incubated



Figure 2.10: Overview of nanosecond work to remove contamination on surface. It was verified that lighter regions correspond to the removal of contamination and dark patches within the irradiated areas are surface and subsurface damage.

with sub-threshold pulses at 10%. The surface film could be removed for powers greater than 2 mW (Figure 2.10) and obvious surface damage is visible above average powers of 6.3 mW.

At a scan speed of 50 μ m/s, the power must be higher than 2 mW to remove a layer from the surface. Given the tenfold increase in the number of effective pulses, it would be intuitive to expect a decrease in the power required to remove the layer but this is not the case. Pre-incubation may have had a small effect. This may also suggest that there is only a small (or zero) incubation, an effect that has been observed on thin films in gold films [72]. Obvious subsurface damage is visible above average powers of 5 mW.
The sample was observed optically with transmitted light to detect changes below the surface. As can been seen in Figure 2.11, an apparently clean surface has substantial damage in the bulk. The subsurface damage is observable in low magnification imaging (Figure 2.10) because of the longer focal depth. The diamond is transparent to the incident irradiation and should not be susceptible to multiphoton effects at such low intensities. Two factors could be responsible for the unexpected damage. First, self focusing could lead to much higher intensities which could initiate multiphoton absorption. Second, the diamond contains some nitrogen impurities and other crystal defects which could act as absorption sites. Although the diamond should be effectively transparent given the low nitrogen conservation, the weak absorption, followed by heating of the very few free carriers through inverse Bremsstrahlung could generate enough heat to create other defects or colour centres. Single substitutional nitrogen is only 1.36 eV from the conduction band edge, making single photon absorption possible at the substitution sites. Furthermore, the lattice contains some extended defects which lead to stress-induced birefringence. These extended defects might also serve as absorption sites.



Figure 2.11: Top: Transmitted light image of diamond after irradiation with nanosecond pulses at a translation speed of 50 μ m/s. Bottom: reflected light image of the same surface semi-superimposed. The darker regions in the transmitted light image indicate the presence of damage embedded in the bulk (160-180 μ m down).

In some cases, the surface may appear to be in good shape optically, but the surface shows signs of damage or roughening when viewed under scanning electron microscopy (SEM). In Figure 2.12, SEM and optical images are shown of the diamond after the contamination has been removed. There is no obvious subsurface damage, as indicated optically (not shown). This roughening could also be leftover surface contamination not removed by the laser pulses. The same roughening is also apparent for higher energies, however, which may suggests otherwise.



Figure 2.12: a) SEM image of a train of 6 ns pulses with 2 μ J of energy per pulse scanned at 500 μ m/s across the contaminated diamond surface. a) Roughening of the diamond surface and removal of contamination can be observed. b) Optical microscope image of the same surface for comparison.

For a scanning speed of 2 mW surface film was removed without obvious damage to the bulk (Figure 2.13). However, surface charging prevented high resolution imaging of the surface.



Figure 2.13: Left: Optical DIC image of region irradiated with 2 μ J, 6 ns pulses. Right: SEM image of the same region. Surface roughening/damage is not evident from this image; however, the cleaning appears to be incomplete (SEM image).

In conclusion, surface contamination on diamond has been removed using nanosecond pulses at 800 nm but the removal causes damage in the underlying diamond. Firstly, the nanosecond pulses cause surface and subsurface damage in the diamond. Second, a surface which appears clean may in fact be covering damage found within the bulk, so surface optical microscopy is insufficient to verify success. Finally, the surface itself may be damaged subtly enough to go unnoticed optically. In the very simplest of terms, diamond, graphite, and amorphous carbon have very similar critical temperatures, which should indicate that attempting a thermal removal process on one will have some effect on the other if they are in contact. For the laser parameters used here, we conclude that nanosecond laser-based cleaning is not appropriate for our purposes.

Chemical etching as suggested by a researcher at Element Six was also attempted. The etching was done in a solution of 70 mL sulphuric acid to 100 mL of hydrogen peroxide and heated to near the boiling point on a standard hot plate. The diamond sample (double side polished) was cleaned for 3 minutes, cleaned with distilled water, inspected, and cleaned a second time for 5 minutes. The surface contamination was partially removed, but it was not possible to remove the it completely. There are more aggressive methods available, which are recommended for future attempts.

Chapter 3

Results

3.1 Survey of ripples following a variety of irradiation conditions

Laser induced ripple formation can lead to a variety of different morphologies and periodicities. The different morphologies may be indications of different mechanisms for ripple formation, as well as different outcomes for the same mechanism. An exploration of the various morphologies is therefore an important consideration in order to identify the most likely mechanisms involved. This section presents findings of the different classifiable ripple morphologies observed on synthetic single crystal diamond and summarizes these findings, along with corresponding periodicity, in Table 3.1.

Normal incidence stationary irradiation at $\lambda = 800$ nm				
Classification	Λ (nm)	N	$\phi (\rm J/cm^2)$	Description
LSFL	≈ 600	5 - 100	1 - 26	\perp , wavelike
HSFL	≈ 250	10 - 20	< 3	\perp , nanoplanar
	~ 170	50 1000	~ 1	\perp , range from smooth
	≈ 170	50 - 1000		to nanoplanar
Normal incidence scanning irradiation at $\lambda = 800$ nm				
Classification	Λ (nm)	$N_{\rm eff}$	$\phi (J/cm^2)$	Description
				\perp , extended, deep
Ordered	120 120	1000 6000	< 1	nanocracks, more bi-
Ordered	150 - 180	1000 - 0000		furcated at high flu-
nanopianes				ence
Normal incidence scanning irradiation of back surface at $\lambda = 800$ nm				
Classification	Λ (nm)	$N_{ m eff}$	$\phi (J/cm^2)$	Description
				Mostly \perp , highly bi-
				furcated in some ar-
HSFL/	150 - 200	a. 19	unlunauun	eas, regions of straight
nanoplanes		≈ 12	UIIKIIOWII	nanoplanes, regions of
				misorientation up to
Other	80 - 110			20°
Normal incidence scanning irradiation at $\lambda = 400$ nm				
Classification	Λ (nm)	$N_{ m eff}$	$\phi ~({ m J/cm^2})$	Description
ICEI	~ 260	0 75	0.0 0.1	\perp orientation, typical
	≈ 200	0 - 75	0.2 - 2.1	wavelike morphology
				Mostly \perp with some
HSFL	≈ 80	8 - 375	< 1	misorientation for
				$N_{\rm eff} \approx 8$
Rough side edge irradiation at grazing incidence scanning via bulk				
at $\lambda = 800$ nm				
Classification	Λ (nm)	$N_{ m eff}$	$\mathbf{E}_{\mathbf{pulse}} (\boldsymbol{\mu} \mathbf{J})$	Description
				\perp orientation, range
HSFL	120 - 190	> 250	12 - 40	from smooth to
				nanoplanar morphol-
				ogy
				Highly bifurcated.
Other	≈ 65	> 250	4 - 12	mostly \perp with some
				regions of misorienta-
				tion

Table 3.1: Summary of ripples results on single crystal diamond from this thesis.

Although surface ripples are diverse in their morphology and periodicity, still two predominant ripples classifications arise, known as low spatial frequency LIPSS (LSFL), and high spatial frequency LIPSS (HSFL) [53]. Other descriptors are introduced to classify additional ripples outcomes. Here, we are categorizing the ripples as HSFL and LSFL based on morphology and periodicity as compared with observations in the literature [21, 53, 56]. It is implicit in the designations of LSFL and HSFL that the ripples were formed via coherent interactions involving the light wavelength. However, since the formation mechanisms of ripples remain a somewhat open question (more so for HSFL), other mechanisms are considered.

3.1.1 Ripple types and morphologies observed on a polished surface following stationary irradiation at normal incidence

Femtosecond laser pulses were focused on a top polished surface in a rough vacuum environment at normal incidence. Pulses were focused using a $5\times$ objective to a $1/e^2$ spot size of approximately 4.5 to 5 μ m. This quantity may vary with day-to-day beam quality and is measured for each individual experimental run. Pulse energy was varied to give a fluence range from 26 J/cm² to 250 mJ/cm² and the spots were irradiated with 1, 5, 10, 20, 50, 100, and 1000 pulses at each energy. No damage was observed below 300 mJ/cm². The resulting craters were then analyzed for periodic structuring using scanning electron microscopy.

LSFL can be observed for a variety of irradiation conditions with some variation in morphology. Following high fluence processing and low numbers of shots, the ripples are less ordered and take on a spikey morphology (Figure 3.1a and 3.1b), while for lower peak fluence the morphology is smoother with a wavelike appearance (Figure 3.1c-e). This wavelike morphology is commonly reported in the literature, and the morphology is similar to that observed previously in diamond [56], and other materials [18, 21, 22, 56, 73], including silicon, glass, metal oxides, compound semiconductors, and graphite.

HSFL can be observed generally for lower fluences and higher numbers of pulses. For a high enough number of pulses, LSFL can no longer be observed, which may be a result of the fluence ranges for which ripples are still visible at a given number of pulses or directly related to feedback mechanisms. The cutoff at which LSFL can no longer be observed is between 100 and 500 pulses, since pulse numbers between 100 and 500 were not tested. On the one hand, this may be due to the range of pulse energies that can produce LSFL since for the pulse energy required to form LSFL at a high number of pulses, too much material removal results and the bottom of the crater cannot be observed by surface electron microscopy. In fact, even if the bottom of the crater could be observed, it is likely that the total energy from the pulses arriving first would not reach the area to be observed so it becomes important to consider what is meant by an irradiation condition (i.e. peak fluence and number of pulses) causing a certain outcome. On the other hand, the feedback mechanisms which are no doubt involved in the formation of surface ripples may play the dominant role, limiting the possibility of LSFL as the number of pulses is increased. The morphologies of selected craters exhibiting LSFL and HSFL are shown in Figures 3.1 and 3.2, respectively. Typically, the morphologies of HSFL are quite different from those of LSFL. However, some cases of LSFL have morphologies that resemble HSFL for processing with very large numbers of pulses, such as observed on stainless steel [74].



Figure 3.1: LSFL features created by normal incidence irradiation with varying pulse energies and shot numbers. The surface is coated with a 5 nm layer of platinum. The double arrow indicates polarization orientation. In (a) and (b), the spikey morphology can be seen in the central region accompanied by extended material removal. In (c) - (e) the features appear smoothed out. Ripple periodicities are (a) 510 nm, (b) 620 nm, (c) 690 nm, (d) 620 nm, (e) 560 nm.



Figure 3.2: HSFL features created by normal incidence irradiation with varying pulse energies and shot numbers. The double arrow indicates polarization orientation. (b)-(e) were imaged with a platinum-coated surface. The characteristic surface layer can be seen flaking off in (a), (b), (c), and (e). Ripple periodicities (a) 260 nm, (b) 260 nm, (c) 200 nm, (d) 190 nm, (e) 150 nm.

A graphical summary of the irradiation conditions which led to HSFL or LSFL is presented in Figure 3.3. Since the x-axis represents the peak fluence, only the features in the central region of the crater have been taken into account. In many of these craters, both HSFL and LSFL can be observed together, with the HSFL in an annular region and the LSFL concentrated in the middle. LSFL has never been observed in the outer region with HSFL in the centre, which indicates that LSFL forms for higher fluences than HSFL.



Figure 3.3: Summary of HSFL or LSFL as the central features in each crater. Note that in many cases, HSFL can be observed surrounding central LSFL regions but the crater features are still classified as LSFL.

In some cases, the two types of ripples (HSFL and LSFL) can be observed overlapping each other. Selected examples of ripples close to the transition between LSFL and HSFL are shown in Figure 3.4. This shows an important feature of the mechanism for ripple formation, suggesting one or both of the following possibilities. It could be that HSFL can form as a result of existing LSFL. On the other hand two distinct mechanisms could be working simultaneously, the crossover observed resulting from the failure of one mechanism to dominate significantly over another.



Figure 3.4: The overlapping LSFL and HSFL features were created by normal incidence irradiation with varying pulse energies and shot numbers. A 5 nm platinum coating on the sample is used to aid high resolution imaging. Low kV imaging prevented charging effects from distorting the image, but partially obscured underlying ripples in (a). The deeper damage feature in (a) was likely a pre-existing pit.

3.1.2 Ripple types and morphologies observed on a polished surface following scanning a beam at normal incidence

Femtosecond laser pulses (6 μ J/pulse) were focused on a polished back surface after propagating through a top polished surface and 500 μ m of bulk diamond (see Figure 2.8). Both the entrance and exit faces were modified, with ripples throughout the modified region. The pulses were focused with a Newport $5 \times$ objective and were scanned at 500 $\mu m/s$ perpendicular to the laser polarization with lines spaced by 30 μ m. The spot size for the 5× objective is 4.6 μ m, so the effective number of shots on the surface is $N_{\rm eff} \approx 12$. However, nonlinear self focusing or self defocusing may have increased this spot size substantially, leading to lower peak fluences and higher effective number of pulses. The modified region on the back polished face is approximately 6 μ m across. However, this width does not remain consistent throughout the length of the scan, as can be seen in the centre of Figure 3.5, where the misoriented ripples do not span the full 6 μ m width. Outside of the central modified region, slightly damaged regions are visible well beyond the 6 μ m-wide lines (shown in Figure 3.5 as pits or scratch-like features). Some milder damage appears to be concentrated in around pre-existing surface imperfections (pitting), which may have influenced the damage threshold. In addition, the top surface sustained substantial surface modification, which may have led to increased scattering of incident light. As a result of these observations, the damage in the periphery could be attributed to stray light scattered by top surface features interacting with existing surface imperfections that render the material more susceptible to laser-induced damage.



Figure 3.5: Back surface modified region and extended area showing damage in periphery (scratch or pit-like features outside the two horizontal lines). The ripples resembling nanoplanes make straight lines at a 20° angle to the scan direction, while the initial polarization direction of the incident beam (vertical in figure) was perpendicular to the scan direction (horizontal in figure).

The back surface exhibits diverse ripple outcomes with periodicities ranging from 90 nm to 200 nm (Figure 3.6) and morphologies that range from appearing somewhat smooth to those that resemble nanoplanes. The ripple orientation has also been tilted by as much as 20° , as can be seen in Figure 3.5, and the tilt is not consistent throughout the modified region.



Figure 3.6: Back surface modified regions exhibiting a variety of ripple polarizations and orientations, indicating a possible variation in polarization orientation and wavelength. In a), b) and c), the pulse energy was 5 μ J and in d) the pulse energy was 10 μ J.

Circularly polarized light pulses were also scanned across the back surface with circular polarization. A quarter-wave plate was placed before the micromachining chamber to achieve this. The pulses were focused using a $50 \times$ objective with pulse energy of 10 μ J at a scan rate of 10 μ m/s. In vacuum, the $50 \times$ objective produces a spot size of approximately 2.5 μ m, although the spot size at the back surface was not determined. The front side sustained no observable damage, while the back polished face was substantially modified. In Figure 3.7 the damage is inconsistent across the surface, possibly due to pulse modification in the diamond bulk (self focusing, nonlinear absorption, plasma-mediated self defocusing). This inconsistent damage has been observed in diamond previously [12] but its cause was not investigated.



Figure 3.7: Back surface modified regions by circularly polarized pulses focused with a 50× objective. The pulse energies were 10 μ J and the scan rate was 10 μ m/s, with a spacing of 5 μ m. The modification is inconsistent due to absorption in the bulk.

The surface features are somewhat circular (the dimensions are mostly independent of orientation) and their dimensions range considerably and are less easily measured than ripples but are typically less than 200 nm in diameter. The central region in some places has no distinguishable periodic structuring (Figure 3.8). As already mentioned, the damaged region on the back surface is inconsistent. While some regions appear substantially modified with evidence of material removal, other regions appear brighter in the image and some areas appear unaffected. The brighter regions may be signs of damage in the bulk.



Figure 3.8: Back surface modified regions by circularly polarized pulses focused with a 50× objective. The pulse energies were 10 μ J and the scan rate was 10 μ m/s, with a spacing of 5 μ m. The morphologies are somewhat circular with dimensions less than 200 nm.

With the 50× objective, the fluence was sufficiently low at the top surface to not cause damage. However, the 5× objective does not have a high enough numerical aperture (NA) to prevent damage at the energies used, so the top surface was damaged and the resulting nanostructuring was investigated. This nanostructuring on the top surface is shown in Figure 3.10. The spot size at the surface was determined using the numerical aperture of the objective and the distance from the focal plane. With NA = 0.1 and focusing on the back surface, the objective must be moved by the thickness of the sample divided by the refractive index, or 208 μ m, assuming we can neglect nonlinear interactions, such as self focusing and self defocusing. This approximation works very well for low numerical apertures. The exact expression (still neglecting nonlinear effects), with variables given in Figure 3.9 is

$$\Delta x = t \frac{\tan(\theta)}{\tan(\phi)}.$$
(3.1)

The approximation used above, for low NA, is arrived at by making the approximation $\tan(x) \approx \sin(x)$, for x small. Then, invoking Snell's law yields

$$\Delta x = t \frac{n_1}{n_2},\tag{3.2}$$

where n_1 and n_2 are the refractive indices of the upper and lower materials in Figure 3.9, respectively.



Figure 3.9: Geometry for calculating the vertical displacement, Δx , required for focusing to the back face of a transparent parallel plate with thickness t, and refractive index n_2 for an objective with numerical aperture NA. The medium above the plate has refractive index n_1 .

Using the extrapolated value for the spot size (20 μ m) and the translation speed of the sample (500 μ m/s), the effective number of pulses (see Section 2.3.2) is approximately 50, and the fluences in Figure 3.10 are approximately 3.2 J/cm², 1.6 J/cm², and 0.8 J/cm², for a, b, and c, respectively. For comparison, the N = 50 threshold fluence is approximately 0.6 J/cm² (a full discussion of the determination of multiple pulse thresholds can be found in Chapter 3.3). It should also be noted that due to the considerable overlap of laser pulses between successive passes, the effective number of shots is somewhat higher than that predicted by the linear treatment given here.



Figure 3.10: Top surface modified regions by linearly polarized pulses focused to 20 μ m spot size (converging beam, 208 μ m before focal plane) with a 5× objective. Higher resolution images of these regions are shown below. The pulse energies were 20 μ J (a), 10 μ J (b) and 5 μ J (c) and the scan rate was 500 μ m/s, with a spacing of 30 μ m.

The morphologies in these regions are varied, with both HSFL and LSFL visible (Figure 3.12) as well as smaller features (Figures 3.11) and 3.14. The central regions of the scan lines were dominated by LSFL ($\Lambda = 560$ nm), while HSFL was most prominent near the periphery (130 nm $\leq \Lambda \leq 200$ nm). A high-resolution image of the periphery of the irradiated region (just outside the view of Figure 3.10b) is shown in Figure 3.11. Here, one can see that the farthest edge of the modified region contained smaller ripples with a periodicity of approximately 90 nm. Figure 3.12b shows the ripples create for lower pulse energies. At these energies, a higher proportion of the irradiated HSFL. The progression of the periodicity in HSFL from higher to lower fluence appears nearly continuous (Figure 3.12b) in contrast with

the periodicity of LSFL, which remains mostly constant (Figure 3.12a). In Figure 3.13, Fourier transform analysis of the surface reveals LSFL components in the region containing apparently only HSFL, and also supports the measured constancy in LSFL by the narrow width of the peak in the spectrum.



Figure 3.11: HSFL with periodicity less than 120 nm, created in the periphery of an irradiated region created by translating a beam across a polished diamond surface at 500 μ m/s. This region lies just outside that shown in Figure 3.10b. At its smallest, which is in the periphery of the irradiated region, the periodicity is approximately 90 nm.



Figure 3.12: a) Top surface LSFL from irradiation with 1.6 J/cm² pulses. $\Lambda = 560$ nm. b) Top surface HSFL from irradiation with 0.8 J/cm² pulses. $\Lambda = 170$ nm near the top (closer to the centre of the irradiated region) and $\Lambda = 130$ nm near the bottom (periphery).



Figure 3.13: a) Fourier transform of Figure 3.12a (LSFL from irradiation with 1.6 J/cm² pulses). $\Lambda = 560$ nm. b) Features corresponding to surface ripples shown in greater detail. c) Centre of Fourier spectrum of Figure 3.12b (HSFL from irradiation with 0.8 J/cm² pulses). $\Lambda = 120-220$ nm. c) Complete Fourier spectrum of Figure 3.12b.

In Figure 3.14, the periphery of the irradiated region shown in Figure 3.10b, structures much smaller than typically observed ripples can be observed. These much smaller structures may be debris re-deposited during the irradiation of the ripples presently being investigated, or ripples created in a pre-existing surface contaminated layer (such as that described in Section 2.4). Ripples in the debris (indicated as region III in Figure 3.14) have a different morphology than the ripples in the diamond crystal (indicated as region I). Instead of deep grooves, the ripples appear as bumps on a flat surface and are quite shallow. This morphology may be a result of the difference in threshold between the diamond and surface debris, which results in preferential removal of the layer of debris.

The periodicity of the nanostructured debris is less than 50 nm in some areas. Given the work by Huang et. al. [18] on graphite, which shows a similarly dominant HSFL and LSFL dichotomy in the ripple periodicities to that observed for stationary surface irradiation presented here, it is plausible that the approximately 50 nm features observed on what is described here as surface debris do not arise as a result of different material properties but as a direct consequence of interacting with a thin film. One could verify the material in which the ripples can be observed by selective etching of the surface layer, as performed in diamond previously [75].



Figure 3.14: Periphery of top surface scanning irradiation at 1.6 J/cm² peak fluence and 500 μ m/s scan velocity. a) Laser-damaged diamond (I), pristine diamond surface (II), laser-damaged surface contaminated layer (III), and virgin surface (IV). b)-c) Closeup of transition to damaged contamination layer. d) Ripples in damaged contamination layer with 50 nm periodicity.

Scanning across the surface with a beam polarized perpendicular to the direction of the scan produces ripples oriented along the direction of the scan, as expected. There seems to be some propensity at very low fluences and perhaps high repetition rates, as in [25], to produce highly ordered planar nanocracks with periodicities on the order of 100-200 nm. In Figure 3.15, we can see deep groove planar type ripples, indicative of the nanoplasmonic mechanism. This morphology is similar to that observed in [25] but lacks the length of nanocracks as well as some of their order. This may be due to their use of higher quality material, a higher repetition rate (250 kHz compared to our 1 kHz) or perhaps superior beam quality. An interesting feature is the singular grooves which seem to extend without neighbouring grooves (Figure 3.15a). Especially noticeable for scanning across a surface is the tendency for ripples to align with existing surface scratches or defects. This occurs for low numbers of pulses and weak laser fluence and has been observed for gentle irradiation conditions previously on SiC [76].



Figure 3.15: The features were created by 150 fs pulse trains scanned at 5 μ m/s with energy of 0.17 μ J per pulse. a) The platinum coating used to aid in imaging can be seen partially filling in the grooves. b) Uncoated sample along the same irradiated path.

A pulse train focused on the diamond surface and translated at constant speed produces a variety of ripples morphologies other than highly ordered nanocracks. Shown in Figure 3.16 are nanostructured grooves irradiated at scan speeds of 10 μ m/s and 5 μ m/s at varying energies. The shorter length of the ripples and fuller coverage in Figure 3.16a-b resemble the typical HSFL that can be seen for stationary irradiation conditions. However, there is also some resemblance to the nanocracks, with the possibility that the cracks formed more readily due to higher pulse energy. At 20 J/cm², shown in Figure 3.16d, a large damage region is created, but the ablation depth is less than that obtained for scans at lower energies, indicating some kind of ablation suppression or microstructure growth (although the structures do not appear ordered). At 6 J/cm², a deep trench is formed with some evidence of ripples near the bottom and in the periphery. Evidence of ablation suppression has been seen previously in diamond [12].



Figure 3.16: Overview of features obtained by scanning a focused beam across the surface. a) and b) ripples with periodicity approximately 150 nm created by irradiation just above the damage threshold (well below the single shot threshold). c) A deep trench created by pulses with fluence more than double the single shot damage threshold. d) Structure growth due to high fluence pulses, which might alternatively be material left behind due to an ablation suppression phenomenon.

3.1.3 Ripple types and morphologies observed on polished surface following stationary irradiation at angled incidence

Ripple periodicities have been shown to depend on the beam's angle of incidence in some cases [21, 26]. In this study, p-polarized interactions are principally investigated, while s-polarized interactions are investigated for grazing incidence only.

The smaller periodicities observed by rough side edge irradiation after propagation through bulk material (Section 3.1.4) call into question whether the effects of high angle of incidence, interaction with a rough side edge, or effects caused by propagating through bulk material may cause the smaller periodicities. Experiments at grazing (85°) incidence were performed to study the effect of angular dependence on the unique structures observed on the rough side edge, including planar ridges with periodicity of 140 nm obtained in [12] and very fine periodic structures with periodicities below 100 nm, shown in Section 3.1.4. A $50 \times$ objective (minimum beam waist approximately 2.5 μ m) focused pulses on a polished diamond surface at 85° from normal incidence. The pulse energy was varied from 40 μ J to 1.4 μ J using reflective neutral density filters in steps of 0.1 optical density. However, the lowest energy for which damage could be observed was 10 μ J at 1000 shots. The number incident pulses at 1 kHz repetition rate was varied from 1000 to 5000. However, due to difficulties imaging the diamond surface at high resolution (a platinum coating was not employed), only samples irradiated with 1000 pulses were imaged throughout the complete range of pulse energies.

An overview of the morphologies observed for grazing incidence at N = 1000shots are shown in Figure 3.17. The fluences stated in the figure are corrected for the projected beam onto a surface oriented at 85° . All ripples have periodicities in the range expected for HSFL (125 - 170 nm) and the morphology appears to be fluence-dependent, with the planar ripples dominating for lower fluences at many hundreds to thousands of pulses. When the pulse energy is sufficiently high to remove substantial amounts of material, ripples can be observed on the sides of the trenches resulting from a p-polarized interaction which causes an abrupt change of orientation.



Figure 3.17: Ripples generated by s-polarized light incident on the top surface at near-grazing 85° incidence. The features have morphologies similar to some of those observed for rough side edge irradiation. Figures (a) and (b): smoother morphology characteristic of higher fluence, $\Lambda = 185$ nm. Figures (c) - (f): planar morphology, $\Lambda = 125$ nm (some ripples as small as 100 nm while others as large as 140 nm). g) Planar morphology but too few ripples to make a measurement of periodicity.

At 85° incidence and 1000 shots with the energy ranges in this experiment, it was not possible to produce the extremely fine features observed for coming out of the bulk through a rough side edge, with the smallest ripple periodicity being about 100 nm. It is therefore likely that the very fine ripples result from the propagation through bulk material or interaction with a rough surface.

Although s-polarized light was not explored for lower angles of incidence, ripples from p-polarized pulses incident from 10° to 85° from normal incidence were investigated. An overview of the outcomes from each angle of incidence is shown in Figure 3.18 with varied fluences and numbers of shots to highlight different ripple types.



Figure 3.18: Ripples generated by p-polarized light incident at varying angles of incidence, where α is the angle away from normal, N is the number of pulses and ϕ is the fluence corrected for projecting onto a surface at an angle. Figures (a) and (b) exhibit HSFL as the dominant features with periodicities of 150 nm and 190 nm, respectively. Figures (c) - (e) exhibit LSFL as the dominant features with periodicities of 410 nm, 380 nm, and 375 nm, respectively. Pulse energies: (a) 0.56 μ J (b) 1.47 μ J (c) 3.25 μ J (d) 1.21 μ J (e) 1.93 μ J. Figure (f) shows the irradiation geometry. In all figures, the horizontal component of the pulse propagation direction is from left to right.

The fluences indicated in the figure were corrected for the projection onto a surface at an angle by multiplying by a factor of $\cos(\theta)$, where θ is the angle of incidence.

The pulse energies corresponding to each subfigure are given in the caption. Corrections for different reflectivity characteristics that depend on the angle of incidence have been implemented in other works [77–79]. This correction may improve comparisons between normal incidence and various angles of incidence but the correction factor varies with free carrier density, which changes throughout the duration of each pulse. Furthermore, this study involves multiple pulse irradiation, which means that the surface morphology changes during the laser treatment. The surface with altered morphology may behave differently than a smooth surface in terms of reflectivity variation with angle of incidence, making corrections based on a pristine surface oversimplified. These considerations combined with other sources of increased error as compared with to normal incidence experiments justify leaving these corrections out of the stated fluences. One place where the correction factor may make a significant difference is in comparing s-polarized and p-polarized conditions near Brewster's angle. However, since detailed comparisons of thresholds is not the aim of this study, we do not include this correction in the fluences stated. For comparison with the literature, the reflectivity as a function of angle of incidence is shown based on a Drude model of the dielectric function of diamond two carrier densities (see equation (1.4)). Using this model, the complex refractive index is calculated (for a chosen carrier density) and is used to calculate reflectivity as a function of angle of incidence. This is done using the Fresnel equation

$$R = \left| \frac{(n+ik)^2 \cos(\theta) - \sqrt{(n+ik)^2 - \sin^2(\theta)}}{(n+ik)^2 \cos(\theta) - \sqrt{(n+ik)^2 + \sin^2(\theta)}} \right|^2,$$
(3.3)

where n and k are the real and imaginary parts of the refractive index, respectively, and θ is the angle of incidence. A plot of reflectivity as a function of angle of incidence
is presented in Figure 3.19. The two carrier densities chosen are the maximum density reached during a single pulse at the ablation threshold ($\approx 3 \times 10^{22}$) and half of that value.

The spatial mode of the beam contained a large lobe for this experiment. Since the beam is non-Gaussian, the D^2 method can only provide an estimate of the spot size. Therefore, the fluences mentioned are an estimate based on a spot size of 10 μ m and are for rough comparisons with other data only.



Figure 3.19: Reflectivity as a function of angle of incidence for a pulse with 800 nm wavelength incident on diamond at three different carrier densities. The dielectric function is calculated using a Drude model and is used to calculate the reflectivity by way of the Fresnel equations for lossy media (TM wave).

The features created for 5 pulses at 60° incidence are unique because they are the only case observed for which ripples could be seen that are parallel to the incident polarization (or the component of the polarization in the plane of the diamond surface). The features are shown in Figure 3.20, where the ripples appear to form as

the result of the alignment of small nano-craters approximately 140 nm in diameter. The periodicity is approximately 160 nm. The nano-craters can also be observed at higher irradiation fluences where they do not align to form ripples. The surface in these cases is dominated by the classic perpendicular ripples which penetrate to a far greater depth into the surface. Compared to LSFL, these parallel ripples appear shallow enough to have formed perhaps only in an amorphous cap layer typically observed on surfaces irradiated with ultrafast pulses under TEM investigation, such as in [12, 57]. Further investigation to measure the ripples depth using AFM could confirm this observation.



Figure 3.20: Ripples generated by 5 p-polarized pulses with a fluence at the sample surface of 1.3 J/cm² incident at 60° from normal incidence. The fluence was calculated by correcting for the projection of the beam onto an oblique surface, without corrections for reflectivity, using a pulse energy of 4 μ J and an estimated spot size of 10 μ m. The average ripples spacing is $\Lambda \approx 160$ nm, parallel to the laser polarization.

3.1.4 Ripple types and morphologies observed on rough side edge following bulk processing

When diamond is irradiated by a beam focused in the bulk and translated out of the rough side edge (see Figure 2.8 in Section 2.3.4), there is a wide range of possible morphological outcomes. For these experiments, three scanning speeds at 50, 10, and $1 \ \mu m/s$ were used with pulse energies ranging from 40 μJ per pulse to energies below which visible damage no longer occurs. An overview of the irradiated regions can be seen in Figure 3.21, a view of the rough side edge of a diamond plate.



Figure 3.21: Overview of modified region in which ripples were analyzed. The trenches are spaced by 100 μ m at decreasing energies (right to left) ranging from heavy processing (removing substantial amounts of material) to below the modification threshold for that scanning speed. Analysis of the trench or modified region on the rough side edge was carried out using scanning electron microscopy.

For high pulse energies, the beam removed a significant amount of material, resulting in the formation of a deep trench in the diamond near the rough surface. For most of their length, these trenches do not extend the length of beam translation, but penetrate only a few micrometers to a few tens of micrometers into the rough side surface, depending on the location in the trench and the pulse energy. The trench formation leads to grazing incidence interactions at many polarization orientations (s- and p- polarized, and components of each). Ripples can be observed throughout most of the trench (examples are shown in Figures 3.22, 3.23, and 3.25) as well as a wider region surrounding it. For lower energies, such a trench does not form, but ripples can still be observed concentrated on the rough side edge, where the beam either exited or grazed the material (it is not certain that the surface texturing was a result of a transmitted beam out of the rough side edge, or the beam interacting at grazing incidence with the rough side edge).



Figure 3.22: Smooth ripple formations in the central region are oriented perpendicular to the s-polarized beam following irradiation of a rough side edge by scanning across a top surface through bulk material. The periodicities of the central features range from 150 nm to 200 nm.



Figure 3.23: Planar ripples may be the result of the formation of nanoplanes in bulk diamond. Left and top: 13 μ J/pulse, 10 μ m/s, in the top image $\Lambda = 130$ nm for the larger features to the left and $\Lambda = 90$ nm for the smaller regions to the right; right and bottom: 17 μ J/pulse, 10 μ m/s, in the bottom image $\Lambda = 150$ nm for the larger features near the centre and $\Lambda = 80$ nm for the smaller regions in the periphery

The classifications of the ripple morphologies and their respective periodicities are outlined and described here, while much of the discussion about the reasons for the particular morphologies can be found in the discussion (Chapter 4). The s-polarized incident beams lead to fine ripples (substantially below incident wavelength, HSFL or finer) in all experimental conditions tested, which is to be expected because of the large number of pulses (from $N_{\text{eff}} = 75$ to over $N_{\text{eff}} = 5000$) incident at each point in the irradiated region. The possibility of these ripples being LSFL with modified periodicity due to feedback from many thousands of incident pulses seems unlikely given that previous reports of this effect indicate that LSFL remain greater than about 0.4λ , which also applies for high angle of incidence [17, 26]. The most common type, those ripples with periodicity in the approximate range of 150 nm to 200 nm (normally attributed to HSFL), can be separated into two morphologies. First, the ripples appear smooth and wavelike (Figure 3.22) and are often bifurcated. In some cases, it appears that the bifurcations are due to the curvature of the trench cut by the beam. The other type appears more ridge-like and tends to occur for lower fluences (Figure 3.23). Here these are called planar structures since they might be attributed to the nanoplanes often observed in transparent dielectrics in the literature [24, 25] and described theoretically by Rajeev et. al. in [58]. Huang et. al. also describe a theory for the formation of planar structures on the surface of a dielectric [18].



Figure 3.24: Planar ripples misoriented with respect to the initial direction of the electric field. Pulses scanned at 10 μ m/s and 13 μ J. The larger features have a periodicity $\Lambda = 110$ nm and the smaller misoriented features have periodicity $\Lambda = 70$ nm.

Other outcomes for s-polarized light, in which the ripples have significantly smaller periodicities (65-90 nm), can be observed for the lowest fluences and may be a result of a beam which has propagated through significant bulk material before interacting with the rough side edge, rather than a beam which has removed enough material to interact with the surface of a deep trench or crater. The morphology of these ripples is planar-like (Figure 3.24). Another feature of these ripples is their occasional misorientation. Whether due to birefringence effects in the material or interaction with surface roughness, some regions have a tilted orientation with respect to the expected ripples orientation. One can estimate the effects of the inherent birefringence of the material on the polarization. The maximum birefringence according to material spec is $n_o - n_e = \Delta n = 10^{-4}$. The maximum phase shift can be calculated by $\Delta \phi = 2\pi \Delta n d/\lambda$, where λ is the wavelength of light in the medium (333 nm), d is the distance travelled through the bulk, which was approximately 100 μ m in the case shown in Figure 3.24. This leads to a total phase shift of less than 11°, which is enough only to introduce some ellipticity to the polarization, making the inherent birefringence an unlikely factor in the misorientation.

The planar structures could be further classified into two types based on periodicity and, arguably, the morphology. As described above, the periodicities are concentrated around 110 nm for some planar structures and 70 nm for others. The smaller ripples also tend to bifurcate more frequently. Over some area, there may be found regions where each type is concentrated as shown in Figure 3.24.

P-polarized interactions are also possible under these irradiation conditions if the fluence is high enough to create a trench. As the beam propagates along one of these trenches, it interacts with a curved surface. This results in a different orientation of polarization for different points in the trench. At the sides, the polarization is oriented mostly perpendicular to the surface, in the middle the polarization is oriented parallel to the surface, and in between, there is a mixed polarization interaction. The morphology of the p-polarized interactions can be seen in Figure 3.22 on the sides of

the trenches. In Figure 3.25, the two ripples types are shown to overlap each other as a result of the mixed polarization interactions. Other cases in which HSFL and LSFL can be observed overlapping are shown in Section 3.1.1.



Figure 3.25: Ripples generated by p-polarized light. The features are overlain with ripples oriented perpendicularly, as would be expected from s-polarized light. The image on the left is from inside the trench, while the image on the left captures both the trench and the laser-textured rough side edge.

A single case of rough side edge processing at very high energy (40 μ J per pulse) and a scanning speed of 1 μ m/s produced ripples with 50-60 nm periodicity (Figures 3.26 and 3.27). In the span of a few microns on the rough side edge, the surface structuring varies substantially, beginning as circular structures outlined by what appear to be deep cracks or voids (Figure 3.26b) giving way to extremely fine and highly bifurcated ripples on the order of 50-60 nm or $\lambda/6n$ (Figure 3.26c), where n = 2.4 is the refractive index of diamond, and finally the ripples become more coherent (although still bifurcated) and increase in periodicity to roughly 90 nm (Figure 3.26d).



Figure 3.26: Heavy processing by a 1 kHz train of femtosecond pulses scanned at 1 μ m/s out of a rough side edge. In a limited region of the trench, the ripples have a periodicity roughly concentrated in the range 50-60 nm. The ripples spacing varies from as little as 36 nm to as much as 72 nm.



Figure 3.27: A closeup of the fine ripples features from Figure 3.26c showing a variation in the spacing of ripples. In this image the variation in the spacing of ripples is from 40 to 72 nm.

3.2 Ripple periodicity as a function of irradiation conditions

3.2.1 Ripple periodicity dependence on fluence and number of pulses at normal incidence

In general, for stationary normal incidence surface irradiation, two dominant periodicity regimes of ripples are observed on single crystal diamond, at approximately 600 nm and 200 nm, as shown in Figure 3.28.



Figure 3.28: Ripple periods measured for different pulse energies and numbers of pulses at an incident wavelength of 800 nm. The irradiation was stationary at normal incidence and the measurements were made for the central region of the crater. In some cases ripples of different periodicity would reside near the crater rim, which were not measured.

Some variation is observed for each regime, with the coarser ripples (LSFL) ranging from 530-690 nm and the finer ripples (HSFL) ranging from 150 - 230 nm. In particular, there appears to be a weak relationship between periodicity and both pulse energy and pulse number. With lower energies and higher numbers of pulses usually leading to finer ripples, although this trend breaks down at fluences above $\approx 10 \text{ J/cm}^2$. Above this fluence, the ripple periodicity decreases with increasing fluence, evident from Figure 3.28 for $N \approx 10$ and $N \approx 20$. In addition, the lower numbers of pulses exhibit less of a decreasing trend in the lower fluences. This could be related to the other commonly observed trend with ripple periodicity within the LSFL regime: decreasing period with increasing numbers of pulses.

At moderately low fluences (less than about a factor of two above the ablation threshold), the ripple periodicity decreases as the number of pulses increases. Figure 3.30 shows the relationship for all pulse energies and for specified pulse energies. At higher fluences a trend cannot be discerned. It should be noted here that, although ripple periodicity is observed to change with increasing number of pulses, it is not implying that the surface material re-organizes necessarily (although this could be possible if the irradiation conditions can support self-assembly). Rather, the assumption is that an existing rippled surface can influence the interactions occurring in a near-subsurface region, which leads to a tighter spacing of the inhomogeneous energy deposition. The result is a deeper crater containing ripples with smaller periodicity than before. In comparison with the fluence dependence of ripples on metals [80], the ripples produced here have a similar range of periodicities, but the fluence range is much larger. On metals ripples could not be observed beyond approximately a factor of 2 above the ablation threshold [80] (based on thresholds for tungsten and titanium



Figure 3.29: LSFL ripple period as a function of fluence for normal incidence and numbers of pulses equal to 10, 20, 50, and 100. On the left is a plot containing ripples periodicity measurements from all fluences for each number of pulses, while on the right, similar fluences are compared against one another.

found in [81] and [82], respectively), while in diamond we see ripples formation for fluences over 10 times the single pulse ablation threshold. This could explain the agreement with their results for lower fluences (an increasing trend with fluence), while this trend is not observed for higher fluences. One explanation might be that the mechanisms for ripples formation at such high fluences may be different. On the other hand, the curvature of the crater could lead to skewed ripples measurement or affect the ripples periodicity due to interactions at oblique incidence.



Figure 3.30: LSFL ripple period as a function of the number of pulses for normal incidence. The graph on the left plots the ripples period at all energies for each number of pulse, which leads to a large spread in the data. The graph on the right contains points only at specified fluences. Ripples could not be measured for N = 100 and $\phi = 5.8$ J/cm².

3.2.2 Ripple periodicity dependence on incident wavelength

For irradiation with 400 nm wavelength pulses, two dominant periodicities were observed (Figure 3.31) with periodicities of 260 nm and 80 nm. It should be noted that the observations were made for the condition of scanning overlapping pulses across the surface, with the effective number of pulses given in the legend. The effective number of pulses is calculated by assuming a Gaussian profile and adding up the total energy deposited at a single point and dividing by the energy in a single pulse. Although this method for obtaining ripple periodicities is somewhat different from that used at 800 nm, the periodicities should be similar to those obtained with stationary irradiation. This claim is supported by ripples observations of select cases with 400 nm and 800 nm light in which the periodicities of LSFL and HSFL observed in scanning and stationary irradiation conditions do overlap. However, the way in which the energy is delivered to the sample differs for the two cases, so direct comparisons of fluence and number of pulses cannot be made.



Figure 3.31: The ripple period is plotted against fluence for various numbers of incident pulses at normal incidence. Ripples were determined by measurements in the central region of each crater (or scanned line). The data points in blue are from irradiation with 400 nm pulses and were measured after translating a beam across the surface with overlapping pulses, while those in red are from irradiation with 800 nm pulses.

Figure 3.31 showing the 400 nm and 800 nm ripple periodicities indicates a strong wavelength dependence, supported by other work on diamond [17, 18, 83] (discussed in detail in Section 4.2). There appears to be a forbidden region of periodicities for both irradiation wavelengths between the two extremes. In addition, for both irradiation wavelengths there is one region of periodicities that is somewhat close to the incident wavelength and one that is close to $\lambda/2n$.

3.2.3 Ripple periodicity dependence on angle of incidence

This section reports the dependence of ripples periodicity on the angle of incidence of radiation with respect to normal incidence.

Fine ripples (or HSFL) do not show a clear angular dependence for surface irradiation with s-polarized light, although only preliminary studies have been carried out. However, the incidence angle may affect the propensity of HSFL formation if the light is p-polarized. One group working on ZnO did find an angular dependence of HSFL periodicity for p-polarized light, although the observed and predicted effects were far smaller than in the case of LSFL (from about 220 nm to 260 nm) [21], which is difficult to discern due to the error in measuring HSFL.

By contrast, LSFL is strongly dependent on the angle of incidence for p-polarized surface irradiation. Surface irradiation with s-polarized light to investigate LSFL has not yet been performed.

The angular dependence of LSFL on diamond is shown in Figure 3.32. As with other observations involving ultrashort pulses, the ripple period is slightly below the irradiation wavelength near normal incidence. The commonly cited trend predicted by Sipe et. al. (namely that $\Lambda = \lambda/(1 + \sin \theta)$) [26] is not closely followed, although the behaviour shows a close relation to the curve shape. It is possible that correction factors related to feedback from a corrugated surface or interactions with an excited surface might be relevant, as explored by some authors [17, 23]. In fact, the classical model does predict other possible functional forms for the angular dependence, for example $\Lambda = \lambda/(n + \sin \theta)$, where n is the refractive index of the sample surface and may vary significantly during the material modification process due to electronic excitation. One particular extension of the classical model shows excellent correlation with these data. This model, described in Section 1.2, leads to equations (1.6) and (1.7). We can determine λ_s empirically by taking the average of LSFL periodicities, we obtain $\lambda_s = 600$ nm. The angular dependence should therefore follow the curve

$$\Lambda = \frac{\lambda}{1.33 + \sin\theta},\tag{3.4}$$

where the quantity 1.33 comes from inserting values into equation 1.6.



Figure 3.32: Ripple periodicity is plotted against the angle of incidence of multiple p-polarized pulse irradiation of a polished diamond surface. The angular dependence is compared with the classical model and a modified version (solid orange and green lines, respectively). Each data point represents an average of all ripples measurements made at the indicated angle of incidence.

With p-polarized light, there is an apparent difference between the type of ripples

that can form at normal and grazing incidence. Although HSFL or similar ripples have been observed for intermediate angles of incidence, HSFL has not been observed for grazing incidence, even for equivalent fluence and shot numbers. In contrast, spolarized light readily generates HSFL at grazing incidence. When the images are analyzed in the Fourier domain, the typical fine ripples (HSFL) at normal incidence and those from s-polarized angular incidence light display a broad frequency spectrum, concentrated around 180 nm. For ripples formed by p-polarized light at grazing incidence, the Fourier domain image shows a sharp peak at the observed 315 nm periodicity along with higher harmonics, which can be attributed to the morphology of the ripples (having sharp troughs and broad crests). This "harmonic" property of the Fourier transform can be observed for LSFL of smaller angles of incidence as well, but usually not for HSFL.

3.3 Damage and ablation thresholds and incubation properties of single crystal diamond

The ablation threshold and incubation properties of type IIa single crystal diamond were investigated with femtosecond laser irradiation at central wavelengths of 800 nm and 400 nm. Polished surfaces were irradiated at normal incidence with stationary beams at varying numbers of pulses and pulse energies. Focusing with 800 nm light was performed with a $5\times$ objective, while a 125 mm planoconvex lens was used to focus 400 nm light.

3.3.1 Determination of thresholds in single crystal diamond

The single shot threshold for single crystal diamond irradiated with a single 150 fs laser pulse at a central wavelength of 800 nm was determined to be 2.3 ± 0.2 J/cm². This value is relatively close to others reported at this wavelength and pulse duration [12, 84]. These authors obtained threshold fluences of 1.9 J/cm² and 1.6 J/cm², respectively, with similar laser parameters.

Ablation threshold experiments on single crystal diamond (at 800 nm) were partially compromised by a surface layer of contamination, described in detail in Section 2.4. The experiment was repeated on a clean sample and both sets of results are presented here. Careful analysis of the ablation craters was therefore necessary to distinguish the damaged diamond from the larger area in which the surface contamination was removed. A combination of differential interference contrast-optical microscopy (DIC-OM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) was used to this end.

Since most of the D^2 analysis was carried out using OM, it is important to correctly identify the crater rim viewed optically. Determining the crater rim for intermediate numbers of pulses (5 < N < 100, where N is the number of incident pulses) is straightforward with the use of DIC-OM, as demonstrated in Figure 3.33. In some cases (e.g. 3.34) an annular region is visible. Here, a comparison is shown between two craters imaged in the optical microscope and scanning electron microscope. Ablation of the diamond occurred in the dark region (as seen optically), which is not obvious from looking at light microscope images alone. The SEM micrograph revealed the optically lighter region to be a removal and texturing of a surface contamination layer on the diamond surface. Further SEM analysis indicates that this region may also



Figure 3.33: OM-DIC image of craters resulting from irradiation with 800 nm pulses focused with a $5 \times$ objective. The crater rim is highlighted by the phase contrast introduced by the Nomarski prism. The faint annulus is assumed to be the early stages of the annular feature observed for N = 1000 and is not included in the crater diameter.

be composed of re-deposited debris and does not correspond to material removal. At N = 1000, the central feature becomes black as a result of increased crater depth and significant HSFL nanostructuring. This was confirmed by correlating crater diameter measurements in the SEM and OM.



Figure 3.34: A comparison between two damage spots imaged with optical and scanning electron microscopy. The beam was focused with a $5 \times$ objective at 1000 shots and pulse energies 0.158 μ J and 0.126 μ J. The dark square in (d) was caused by electron beam contamination in the SEM during higher magnification.

A similar comparison was performed for N = 1. This comparison is shown in Figure 3.35, which shows the many different rims that would be possible to track for the crater diameter. The SEM comparison shows that the outermost ring is a result of a partially removed layer of contamination, much of which had flaked off between the imaging in the different microscopes. This was probably due to handling and cleaning of the sample many times prior to applying a coat of platinum to the surface to improve imaging capability. A rim can be detected in the SEM, which corresponds to the boundary of the second ring.



Figure 3.35: A comparison between two damage spots imaged with optical and scanning electron microscopy. A single pulse was focused with a 5× objective, with pulse energies 10 μ J (a, c) and 6 μ J (b, d). A rim is visible in the SEM image which corresponds to a light disk in the optical image. This feature was followed for the diameter analysis.

For added confirmation that we follow the feature corresponding to an ablation crater, AFM analysis was performed on a crater on a surface free from contamination. Figure 3.36 shows the depth profile indicating a maximum crater depth of approximately 40 nm. A comparison of diameter of the rim as measured under AFM and the suspected rim as observed under DIC-OM finally confirms that the correct feature has been identified (Figure 3.37).

3.3.2 Incubation properties of single crystal diamond

Figures 3.40 and 3.38 are plots of the crater diameters squared against the pulse energy for each crater at different numbers of incident pulses. Section 2.3.5 describes



Figure 3.36: AFM depth profile for a crater left by a single pulse at 9.9 μ J of energy focused by a 5× objective. Red cursors are positioned at the crater rim. Some debris on the sample surface is responsible for the surface spikes in the height, while pitting inherent in the surface is responsible for the spikes in depth.

in detail how we can extract a threshold energy, spot size, and a threshold fluence. These plots show how each ablation threshold is determined.

A D^2 plot for the irradiation of diamond at $\lambda = 800$ nm is shown in Figure 3.38. This experiment was performed on a sample contaminated by a thin film on the surface, discussed in Sections 3.3.1 and 4.1. Error bars are addressed in the discussion (Section 4.4). It is clear that a reduction in the ablation threshold occurs for an increasing number of incident pulses, consistent with past observations on this and other materials.[33, 78]. The craters resulting from the highest energies violate the linear trend and are excluded from the analysis, although this phenomenon is not fully understood. It is possible that the high fluence can lead to a complex interaction in



Figure 3.37: AFM depth profile for a crater left by a series of single pulses with decreasing energy right to left focused by a $5 \times$ objective. Red cursors are positioned at the crater rim. Measurement of the crater in each imaging modality confirm the observable feature in the LM corresponds to the actual crater rim.

which energy is not deposited locally or the assumption of a Gaussian profile breaks down near the tails of the pulse.

Due to the presence of surface contamination, the experiment was repeated on a clean sample. A spatial filter was also employed in an attempt to improve the beam quality. However, the inherent pointing stability of the laser system may have been an issue, which prevented the beam from remaining stably focused through the pinhole, leading to the observed energy fluctuations throughout the experiment. The data is shown in Figure 3.39. The measured spot size in this experiment is $5.51 \pm 0.14 \ \mu$ m, which is significantly larger than that found in the run on the dirty sample. The opposite is expected due to the cleaner beam profile. However, the smaller spot size



Figure 3.38: D^2 data for shots 1 to 1000 at wavelength $\lambda = 800$ nm using a 5× objective. These data are used for extracting threshold fluences for each number of shots, as well as a spot size. The single shot spot size as determined from the slope of the N = 1 fit is $4.36 \pm 0.14 \ \mu$ m.

in the first experiment was confirmed by a calibration run on a clean piece of silicon, which suggests that the spatial filter has introduced some other changes which lead to the larger spot size.

The D^2 plot for an incident irradiation wavelength of $\lambda =400$ nm is shown in Figure 3.40. In this experiment a half-wave plate and polarizer combination was the primary pulse energy control instead of the use of reflective neutral density filters as used in the experiments at $\lambda = 800$ nm. The improvement in linearity is due to using a focusing optic with a larger minimum spot size on a cleaner sample ($\omega = 11.35 \pm 0.13 \ \mu$ m). The larger spot leads to a reduction in the relative error in the crater measurement and there appears to be less random deviation from linearity, which could be due to the



Figure 3.39: D^2 data for shots 1 to 1000 at wavelength $\lambda = 800$ nm using a 5× objective and a spatial filter to improve the spatial mode. These data are used for extracting threshold fluences for each number of shots, as well as a spot size. The single shot spot size as determined from the slope of the N = 1 fit is $5.51 \pm 0.14 \ \mu$ m.

absence of the thin film that contaminates the sample used for the first experiment at $\lambda = 800$ nm. A significant energy drift was not detected, spatial filtering was not employed and the sample was observed to be clean.

Figures 3.41, 3.42, 3.43 show the dependence of the ablation threshold on the number of incident pulses in synthetic single crystal diamond at $\lambda = 800$ nm and 400 nm. The weighted fit was performed for the power law model where the incubation coefficients (ξ) are measured to be 0.71 ± 0.02 and 0.73 ± 0.04 for $\lambda = 800$ nm and 0.73 ± 0.02 for $\lambda = 400$ nm. The slope of the linear plots is $1-\xi$. A detailed description of the fitting procedure can be found in Section 1.2.5. An exponential model has been proposed to describe the incubation phenomenon and there is evidence to support it



Figure 3.40: D^2 data for shots 1 to 1000 at wavelength $\lambda = 400$ nm using a 125 mm focal length lens. These data are used for extracting threshold fluences for each number of shots, as well as a spot size. The single shot spot size as determined from the slope of the N = 1 fit is $11.35 \pm 0.13 \ \mu$ m.

[33]. The exponential model proposed by Ashkenasi et. al. has a characteristic k value which indicates the strength of the incubation behaviour. In the materials tested by Ashkenasi et. al, this value ranges from 0.07 for LiF to 0.9 for YLF and an intermediate value of k = 0.25 was found for α -SiO₂. Although this model has been somewhat successful, the data here is not appropriate for an exponential model, which can be shown by plotting residuals of the data with the fit (see discussion in Section 4.4).

The idea of a baseline threshold, an ablation threshold that is approached as $N \to \infty$, could be extended to the power law model. The introduction of a baseline to the data improves the fit slightly (according to a summation of the residuals, fits



Figure 3.41: The dependence of ablation threshold on the number of shots for 800 nm incident light. The curve is a power law fit giving an incubation coefficient of $\xi=0.73$.

with the baseline applied are shown in Figure 3.44) but the incubation coefficient necessarily changes as a result indicating different incubation behaviours for the different wavelengths. The baselines that minimize the residuals for the 800 nm work on a contaminated sample, the 800 nm work on a clean sample and the 400 nm work on a clean sample are 360 mJ/cm², 280 mJ/cm², and 60 mJ/cm², respectively. The new incubation coefficients are 0.44 ± 0.02 , 0.54 ± 0.02 , and 0.70 ± 0.02 , respectively. However, the infinite pulse thresholds should be the same for the clean and contaminated samples (or very near to) since the surface layer has the effect of removing a certain number of pulses, which has less effect as the number of pulses increases. Fixing the baseline at 280 mJ/cm² for the data from the contaminated sample leads to an incubation coefficient of 0.57 ± 0.02 , which is in agreement with the data from the clean sample. If a baseline is introduced, it suggests that the incubation property



Figure 3.42: The dependence of ablation threshold on the number of shots for 800 nm incident light. The curve is a power law fit giving an incubation coefficient of $\xi=0.71$.

of diamond is wavelength-dependent but this effect is not observed without the baseline. Note that in Figure 3.44, a common baseline is chosen for the two experiments at $\lambda = 800$ nm but this may not necessarily be the case if the surface layer plays a more complex role than considered here. The plots of data shifted by a baseline are intended to illustrate the improved fit.



Figure 3.43: Incubation behaviour of damage thresholds for incident irradiation at λ = 400 nm using a 125 mm focal length lens.



Figure 3.44: Incubation behaviour of diamond assuming a baseline for the ablation threshold. The slope of each line shifts to give a new incubation coefficient indicated on the respective graph.

Chapter 4

Discussion

4.1 Sample Quality

The sample surface quality of the single crystal diamond plates may have had an effect on the laser-material interactions. The samples obtained from our supplier were covered in small pits ranging from a few tens to a couple hundred nanometers in depth. Also, a thin (tens of nanometers) film, the origin of which is unknown, can be observed on a large portion of the surface.

Sharp features, such as cracks, pores and crevices cause electric field enhancement of incident radiation, locally reducing intensity threshold for carrier excitation and therefore ablation thresholds [70]. This effect is pronounced for feature sizes below the laser wavelength, such as the pits in the diamond samples used here (see Section 2.4). The effect of the pits on ablation threshold measurements is most pronounced for irradiation very near the threshold and for multiple pulse irradiation. As shown in Figure 4.1a, for single shot experiments, there is no evidence that pitting had an effect on the crater diameter overall. This claim is based on the locality assumption

that D^2 measurements are based on and the fact that the field enhancement effect for the pits is highly localized. However, for multi-pulse irradiation, the pitting defect can grow substantially, causing the formation of a crater where one might not have formed without the pits. There is evidence that ripples formation can be seeded from these pits, perhaps extending ripples along their crevasses through feedback mechanisms. In Figure 4.1b, the initial stage of ripples formation can be seen extending horizontally from a pit in the surface. This leads one to conclude that the pit provided a local field enhancement effect for ablation to take place. Evidently, in near-threshold multiple pulse irradiation, ablation gives rise to a rippled surface, indicating a connection between the ablation threshold phenomena and ripples formation. The progression of this effect is shown in Figure 4.1c, where the irregular spatial distribution of the damage area suggests that damage may have been seeded by existing pits on the surface. After each pulse, a slightly larger crevasse (initially a pit, gradually becoming the ripples) provides the necessary field enhancement for further damage to occur. This is a speculative, albeit plausible effect of pitting on the damage threshold for multiple pulse irradiation. Performing ablation threshold experiments on higher quality samples will circumvent these issues. On new samples, the film cannot be detected, but pitting can still be observed on samples of equal quality. Other new samples have been acquired, which are free of pitting and have much lower impurity concentrations.



Figure 4.1: Effect of surface pitting on ablation characteristics. a) Single pulse diameter measurements appear unaffected by pitting. Note that in (a) the sample is tilted 50° for imaging. The fine dotted line marks the crater rim, with a roughening feature prominent in the centre, possibly indicative of a different ablation mechanism than that observed in the rim. In (b) - (d) the effects of pitting on multiple pulse irradiation is evident, in particular by acting as seeding points for ripples formation. In (d) the most damage is delivered off-centre.

The unwanted surface film (Section 2.4) is another potential factor influencing the calculated ablation thresholds. This thin film may provide shielding for the diamond below, increasing the measured ablation threshold. Another effect postulated by G. Miyaji in [85] is that thin carbon films act as a conducting surface to assist surface plasmon generation, which could affect ripple formation on the surface. This may

lead to ripples forming with a higher propensity than what should be expected on a virgin diamond surface.

Strain-induced birefringence, shown to occur in synthetic CVD diamond plates from extended defects [11] may affect the polarization of light that travels through a substantial amount of bulk material. In some circumstances, the ripple orientation was observed to be tilted by a few tens of degrees away from perpendicular to the incident electric field, such as in Figures 3.5 and 3.24. However, it was shown in Section 3.1.4 that it is unlikely that this rotation is a result of the inherent birefringence alone.

4.2 Ripples from surface experiments

Despite extensive research into the mechanisms involved in laser-induced ripple formation, the subject remains controversial. This discussion will address similarities and discrepancies between the results presented here and those in the literature, and will outline the relative suitability of the existing proposed mechanisms for explaining the observations presented in Chapter 3.

At normal, stationary beam incidence the morphological results of HSFL and LSFL coincide well with most previous reports in the literature [12, 18, 83]. Diamond produces ripples which are often bifurcated and lack order that is more readily achievable in some compound semiconductors [21, 56]. However, under certain conditions, highly ordered planar ripples have been observed on diamond [25]. The two most commonly observed ripple periodicities for the parameters tested are in general agreement with the literature, being either somewhat near (but strictly less than)
the wavelength of the incident light pulses or in the neighbourhood of half the incident light wavelength divided by the refractive index of diamond at the incident wavelength [18, 53]. Similar results were obtained by several groups who found the same semi-discrete property of ripples to fall under either the LSFL or HSFL category [12, 18, 83].

HSFL periodicities from 170 nm to 190 nm were obtained for irradiation with femtosecond pulses at 800 nm in previous work, depending on incident fluence [18]. The smaller periodicities were obtained with a near-threshold fluence of 1.9 J/cm² while the larger periodicities had a slightly different morphology and were generated with a fluence of 2.8 J/cm². The morphology was similar to the "smooth" morphology shown in e.g. Figure 3.22, and the periodicities are within the range of HSFL found in this work. The finer features are planar in morphology, similar to that observed for 1000 pulses or in the periphery of craters for lower numbers of pulses (see e.g. Figure 3.2). The same group measured LSFL periodicities in diamond in the range of 640 to 480 nm for pulse numbers 10 to 100 [17] at a central irradiation wavelength of 800 nm. They also measured LSFL at 400 nm for 1000 pulses but it cannot be compared with the present work since the fluences required to achieve LSFL according to Huang yielded craters too deep and narrow to appear readily in the microscopic analysis due to the use of a smaller spot size. The range of LSFL periodicities matches well with the results presented here.

In related work, Hsu et al. found HSFL periodicity at 210 nm for 50 pulses in the peripheral region surrounding LSFL in the centre [12]. Their work also confirmed that the ripples are composed of a pristine single crystal diamond core capped by an ultra-thin layer of amorphous carbon. LSFL periodicities were found to be between 600 and 650 nm, which is within the range of values presented here.

HSFL and LSFL have been obtained on diamond at shorter wavelengths, with a train of approximately 100 pulses at 248 nm central wavelength producing ripples with periodicity as small as 50 nm [83], close to the 47 nm periodicity predicted by the relation $\Lambda = \frac{\lambda}{2n}$, where n = 2.64 is the refractive index of diamond at the incident 248 nm wavelength. This group found LSFL with 250 nm periodicity throughout the irradiated spot. However, the claimed periodicity is difficult to verify with the manuscript since the scale bars of the images indicate that the LSFL periodicity is 200 nm in one case and 320 nm in another. In general, wavelength dependence is suggestive of some kind of interference effect, although the self assembly models do predict a periodicity dependence on absorption depth, which is expected to change with wavelength.

Selected ripples outcomes in dielectrics other than diamond, which have been presented in the literature, are summarized in Table 4.1. The ripples outcomes on diamond, which have been presented in the literature, are summarized in Table 4.2.

luctors	Proposed model	self organization				SPP excitation and	coupling to surface	corrugation	Interference between	incident radiation	and surface scattered	Waves	SPP excitation and	coupling to surface	corrugation	Classical model, mate-	rial properties altered	by carier density		مامعوام	TOTICODIA	
d semicono	/ ⊤	LSFL:	HSFL:⊥	LSFL:	HSFL: L						-										-	
lielectrics an	$\lambda/2n~({ m nm})$	272		276				174		066	077						79			205	205	
outcomes for c	$\Lambda_{ m HSFL} \ (m nm)$	230		200 - 400				170		035	700						90			200 - 280	160	
select ripples	$\Lambda_{\rm LSFL} \ ({\rm nm})$	600 - 900		500 - 800		096 - 009	425			200	00		770 - 1150	350 - 450	160 - 225		337 - 343		500 - 720	630 - 730		345 - 480
mary of	τ (fs)	120		150		30000	30000	125		150	00T		30000	30000	30000		40		125	200	150	30000
4.1: Sum	$\lambda \; (\mathrm{nm})$	800		800		1280	532	800		775			1280	532	266		400			800		532
Table ⁴	$n(\lambda)$	1.47		1.45		≈ 3.5	2.33	2.30		1 76	0			2.67			2.54			1.95		≈ 2.7
	Material	${ m BaF}_2[16]$		Fused silica	[86]	GaAs [17]	Graphite	[17, 18]		Samhira[87]	napritte [10]		Si [17]	SiC [17]	7		TiO_2 [73]		$O^{n}Z$	[17 91 88]	[UU (12 (11)	ZnSe [17]

Table .	4.2: Sumi	mary of	select ripples	outcomes for α	liamond and	diamond-li	ke carbon films
Material	$\lambda \ (nm)$	τ (fs)	$\Lambda_{\rm LSFL}$ (nm)	$\Lambda_{ m HSFL} \ (m nm)$	$\lambda/2n \; (\mathrm{nm})$	<i>⊤</i>	Proposed model
Single crystal diamond [17]	800	125	400 - 600	I	I		SPP excitation and coupling to surface corrugation
Single crystal diamond [25]	800	120	I	146	167	_	Nanoplasmonics: growth of nanoplanes extending to surface
Single crystal and poly- crystalline diamond [83]	248	380	≈ 250	50 - 100	51		Interference between scattered surface wave and incident radiation
Single crystal diamond [18]	800	125	I	170 - 190	167	4	SPPs initiate groove formation, followed by cavity mode ex- citation in grooves, field enhancement and feedback effect
Single crystal diamond [12]	800	170	600 - 650	210	167		None
Industrial di- amond [84]	800	100	610	I		-	None
DLC film (500 μ m thickness) [85]	800	100	I	120	167	-	SPP interference mediated by thin graphite layer caused by initial laser pulses

For irradiation of a top polished surface at normal incidence, the orientation of all ripples in single crystal diamond is perpendicular to the direction of the polarization of the incident laser pulses. For more complicated irradiation conditions, other orientation conditions are possible. For example at a high angle of incidence (Figure 3.20) the ripples form parallel to the polarization and after translating through bulk material (Figures 3.24 and 3.5) the ripples are slightly misoriented from perpendicular to the polarization. This observation is contrary to the typically expected "dielectric" behaviour observed in glasses and other crystals [19, 73, 86, 89] and has been previously observed in diamond. However, ripples parallel to the incident polarization have been reported in large grain size polycrystalline diamond film [87, 90]. A suitable theory should be able to explain key features of the ripples observations, including:

- 1. Polarization dependence of ripple orientation
- 2. Periodicity dependence on fluence, number of incident pulses (N), wavelength, and angle of incidence
- 3. Morphology
- 4. Material dependence (e.g. propensity for HSFL formation)
- 5. Material independence (e.g. LSFL, universality)

In general, there is disagreement regarding the formation of classical ripples (LSFL) and insufficient evidence and theoretical rigour to describe the formation of HSFL and other more complex nanostructures. There are cases in which neither the classical models nor the self assembly models seem appropriate, for example in the formation of nanoplanes in dielectrics [58, 58]. However, the formation of surface ripples still

receives significant attention and most discussion of formation mechanisms is focused on that phenomenon. Therefore, the above list is directed primarily at surface ripples.

Both self assembly models [65] and models based on the classical theory developed by Sipe *et. al.* [26] predict a polarization dependence for ripples formation. In the self assembly models, the polarization dependence arises because of an asymmetrical energy deposition due to the electron drift following the electric field of incident laser pulses [65]. This model can explain the ripples which align perpendicular to the polarization but no theory has vet been put forth that describes the formation of ripples parallel to the polarization as in the case for some dielectrics [19, 73, 86, 89]. On the other hand, classical models have rigorously predicted that parallel ripple orientations are possible, at least for the LSFL case [26]. However, the occurrence of ripples oriented parallel to the polarization seems to be less common, except in some dielectrics, most notably glass [86, 89]. The case for HSFL is more heuristic, although evidence for coupling to surface electromagnetic waves such as surface plasmon polaritons or dipole-related waves for some cases in dielectrics has support as well from sources which indicate the importance of free carrier density on ripples orientation (either parallel or perpendicular) [86]. Recall that surface plasmon polaritons are forbidden on dielectric surfaces but that the high carrier densities initiated by intense ultrashort pulses can prepare a surface in a transient metallic state [41, 42].

Ripple periodicity is not well understood from the standpoint of self assembly models. At their surface, the models predict that ripple periodicity should be independent of wavelength and angle of incidence but dependent on fluence [60]. One attempt to quantify the ripple periodicity has been made, which attempts to relate the periodicity to factors involving absorption depth and surface temperature [65]. The model involves too many free variables for an outright prediction of periodicity, but the predicted exponential behaviour can be supported experimentally. Some experimental comparisons are made that show increasing complexity and size of surface structuring as the total irradiation dose increases [62]. Although the precise size of the features cannot be predicted, the nature of the structure evolution has been supported by experiments. However, the fluences used in those experiments are much higher than those used here [62]. The higher complexity of some features may indicate a large window of applicability of the self-assembly models, perhaps involving conditions which lead to a thick melt layer or higher average temperatures resulting from exposure for longer timeframes.

The classical models have had some success predicting ripple periodicity and in particular the behaviour of periodicity as a function of angle of incidence [26]. In addition, extensions of this theory have been successful predicting ripple periodicity as a function of numbers of pulses [17] and incident fluence [80]. Experimental verification of the angular dependence has been shown in [27] on semiconductors and dielectrics. The extension to ripples created by femtosecond pulses, which have reduced periodicity, has been shown on dielectrics in [21] and on metals in [91]. Classical models also predict a dependence on incident wavelength. This dependence is not so clear-cut because of the occurrence of the two ripple regimes, LSFL and HSFL. However, in this thesis, a substantial change in ripple periodicity is observed between 800 nm and 400 nm irradiation. In addition, a survey of reports in the literature yield a strong angular dependence of the ripples periodicity in the incident irradiation wavelength range of 248 nm to 1064 nm. Self assembly models predict various morphologies including bifurcations, circular polarization outcomes, loosely describes ripples lengths. On the other hand, the classical theories mostly describe the ripples periodicity without weighing in on morphology. However, certain features such as angled bifurcating lines appearing in craters and other features, which can be tracked through Fourier analysis have been predicted by extending classical models with dynamic material optical properties [22]. Coherent models based on field enhancement effects inside a cavity have been used to describe HSFL and these models predict the deep narrow trenches often characteristic of HSFL on dielectrics and other materials such as graphite [18].

Nanoplasmonics is a complementary theory to the self assembly models and the classical models (and their extensions). This class of theories specifically applies to bulk modification but could be extended to surface modification if bulk effects propagate through to a surface. In addition to providing a plausible explanation for the periodicity, this theory accurately describes the deep narrow trenches that are often associated with HSFL, much like those theories involving cavity field enhancement mentioned above. In addition, there are some cases (such as Figure 3.15), in which one narrow trench appears to run away from the rest, following no periodic nature at all. This is a plausible outcome for a beam that is very near to threshold.

4.3 Ripples from bulk experiments

Irradiation of a rough side edge (irradiation geometry shown in Figure 2.8) has led to new observations, which have not yet been published to our knowledge. Although there has been a report of ripples with a periodicity of 50 nm after irradiation of a diamond surface with femtosecond laser pulses, the ripples were formed in a surface layer of graphitized material, evidenced by their removal by an etching procedure [75]. However, the ripples presented here (in Section 3.1.4) appear similar to those shown to be composed of the original diamond material based on microscopic observation [12], although etching has not been carried out to confirm this. At the very least, it appears that these ripples did not form in a thin surface contamination layer based on the absence of what a desorbed layer of film on the surface (marked by a thinning of the rippled area giving way to a flat surface below, see e.g. Figure 3.14). Rather, the ripples shown in Figures 3.24 and 3.26 are the dominant features in their respective regions. If the sub-100 nm ripples shown here prove to be composed of single crystal diamond in a manner similar to the HSFL ripples presented, for example in [12], they will be the smallest ripples reported in the crystalline material relative to the incident laser wavelength to our knowledge. Cross sectional transmission electron microscopy or micro-Raman analysis can be used to confirm crystallinity [12, 18, 92].

The conditions for these ripples formation are unconventional in that considerable material processing was involved in their formation. It has been shown that high intensity laser interaction with some materials results in supercontinuum generation [93]. In isotropic materials second harmonic generation is suppressed by a lack of phase matching between the fundamental and generated second harmonic. However, interfaces of isotropic materials do allow a reflected and transmitted component of the second harmonic (a direct consequence of the discontinuous refractive index and electric field perpendicular to the surface) [94]. Diamond also has a relatively high third order nonlinear susceptibility, leading to the possibility of third harmonic generation. If this could be demonstrated, it would support the evidence so far that fine ripples form at the incident wavelength divided by twice the refractive index. That is, the third harmonic of 800 nm is 266 nm, divided by 2n gives ≈ 50 nm.

4.4 Incubation

The single pulse thresholds measured here are substantially different for 800 nm and 400 nm wavelengths (2.3 J/cm² for $\lambda = 800$ nm, and 1.6 J/cm² for $\lambda = 400$ nm). The difference must be related either to the absorption efficiency or the absorption depth of the total pulse energy, since a certain energy density must be exceeded within a near-surface layer in order to cause ablation. There are several possibilities for higher absorption efficiency of 400 nm light. First, the multiphoton absorption rate may be different for the two wavelengths. Currently there are no reports of a measured four-photon cross section of diamond in the literature, so this cannot be ascertained. Second, the temporal pulse profile may be altered during second harmonic generation, although it is not clear whether the pulse would become shorter or longer. Since the conversion is proportional to the intensity squared, the higher intensity peak will be preferentially converted and pulse durations can shorten for longer (e.g. nanosecond) pulses. However, ultrashort pulse durations are very sensitive to dispersion effects, which could counteract this pulse duration contraction. If the pulse did shorten during conversion, it could lead to a higher conversion efficiency since, in general, absorption rates are dependent on laser intensity. Another efficiency benefit of the frequencydoubling process could be weaker ancillary pre- and post- pulses, though only one or two percent of the energy can be found in these pulses, so the maximum efficiency benefits are minimal. The reflectivity at the two wavelengths may also play a role, since the higher carrier densities created will lead to the reflection of a substantial portion of the pulse. Finally, the absorption mechanisms may vary slightly due to the Keldysh theory of nonlinear absorption. Since the 800 nm has a lower frequency, higher electric field amplitudes are required to reach the equivalent intensity from a 400 nm pulse. This has an effect on the band structure, leading to tunnelling ionization, rather than multi-photon ionization (see Section 1.2). The Keldysh parameter indicates that some combination of tunnelling ionization and multi-photon ionization is taking place above the single pulse ablation threshold for diamond at $\lambda = 800$ nm, which may lead to further discrepancy in the absorption efficiency between the two wavelengths.

4.4.1 Error considerations

In this section we consider the various sources of error in the incubation experiments and explain how the fitting procedure takes these errors into account. For incubation results we should be concerned with both the measurements of the diameters of the craters and the energy contained in each pulse.

Measurements of power fluctuation were made over time scales of several hours. Recent measurements taken around the time that the present experiments were performed indicates fluctuations no greater than +/-3% (standard deviation) over a few hours. Since the power meter measurements involved averaging a 1 kHz pulse train over 100 ms intervals, the method was unable to resolve pulse-to-pulse instabilities. A fast photodiode and oscilloscope were employed to reveal fluctuations of about +/-1.5%, suggesting that the pulse energy is at least stable within the +/-3% indicated long term. The power meter reading is also a source of error but this error should be systematic if the same meter (set to the same scale) is used for all measurements and therefore not affect the relative thresholds between different shot numbers and not affect the measurement of an incubation coefficient.

Craters were imaged using differential interference contrast optical microscopy (DIC-OM) and the diameters were measured in Corel Draw using a calibrated measurement tool. In the best imaging efforts, measurements are precise to within four or five pixels, which works out to approximately +/-400 nm. This equates to nearly 20% error for the smallest craters, but less than 3% for the larger craters. For some images, the error is larger, approaching 700 nm.

Another source of error is the shape of the beam, which is assumed to be Gaussian, but as can be seen from the beam profiles is demonstrably not Gaussian but is some approximation thereto. Therefore, the beam may contain hotspots, leading to higher peak fluence than expected. Furthermore, if the shape is not Gaussian then the D^2 method breaks down at the tails of the pulse (which might have an effect for higher fluences). For this reason, fairly low fluences were used for the analysis, where the pulse is expected to more closely approximate a Gaussian shape.

Finally, the inherent spatial jitter in the laser system and optics that follow could lead to a smearing of the beam for multiple pulse irradiation. Some spatial instability is suspected due to the power fluctuation observed when using the spatial filter apparatus. This jitter could be one of the causes of the increase in the slopes of the D^2 plots for multiple pulse threshold experiments, which directly imply a larger spot size for multiple pulse irradiation. If the beam is moving around on the sample surface an effective larger spot size is reasonable to expect given the spread in total energy over a larger area. Despite this possibility, all threshold fluences were calculated using the single shot spot size. If this effect is taken into account and fluences are calculated using the spot size for each number of pulses, the shift will be to lower thresholds for multiple pulse thresholds and it will not affect single shot threshold measurements.

Error bars were determined as follows. On the horizontal axis, the uncertainty in $\ln(E)$ is determined by error propagation from the uncertainty in E.

$$\frac{\sigma_E}{E} = 3\% = 0.03$$
$$\sigma_{\ln(E)} = \left| \frac{\partial \ln(E)}{\partial E} \right| \sigma_E$$
$$= \left| \frac{1}{E} \right| \sigma_E$$
$$= 0.03$$

On the vertical axis, the known uncertainties for the crater diameters D_1 and D_2 are propagated to the square of the geometric mean of the two diameters, or equivalently, D_1D_2 . Since the diameter measurements are independent, the uncertainty of the squared diameter is as follows.

$$\sigma_{D_1D_2} = \sqrt{\left(\left|\frac{\partial(D_1D_2)}{\partial D_1}\right|\sigma_{D_1}\right)^2 + \left(\left|\frac{\partial(D_1D_2)}{\partial D_2}\right|\sigma_{D_2}\right)^2}$$

However, $\sigma_{D_1} = \sigma_{D_2}$ and will be denoted σ_D , which leads to

$$\sigma_{D_1 D_2} = \sigma_D \sqrt{D_1^2 + D_2^2}$$

This uncertainty depends on the crater dimensions, which is evident in the D^2 plots.

Since the error varies for each point, a weighted fit was implemented in order to extract thresholds, with weights $w_i = \sigma_i^{-2}$, for each $y_i \pm \sigma_i$, where y_i is written in place of D^2 and σ is written in place of $\sigma_{D_1D_2}$ for brevity. Fitting parameters were calculated using a weighted least-squares fit. For a linear fit of the form y = A + Bx, the parameters A and B were obtained by

$$A = \frac{\sum w_i x_i^2 \sum w_i y_i - \sum w_i x_i \sum w_i x_i y_i}{\Delta}$$
$$B = \frac{\sum w_i \sum w_i x_i y_i - \sum w_i x_i \sum w_i y_i}{\Delta},$$
where $\Delta = \sum w_i \sum w_i x_i^2 - \left(\sum w_i x_i\right)^2$

The uncertainty in the slope is obtained by

$$\sigma_B = \sqrt{\frac{\sum w_i}{\Delta}}$$

The uncertainty in the x-intercept is obtained by calculating the 68.2% confidence interval for the fit line and finding the two x-intercepts of this curve. The $(1-\alpha)100\%$ confidence interval is given by

$$y = A + Bx \mp t_{n-2,1-\frac{\alpha}{2}} \sqrt{\text{MSE} \cdot \left(1 + \frac{1}{n} + \frac{(x-\overline{x})^2}{(n-1)\sigma_x^2}\right)},$$

where $\text{MSE} = \frac{1}{n-2} \sum (y_i - A - Bx_i)^2$

is the mean squared error of the dependent variable y, and $t_{n-2,1-\frac{\alpha}{2}}$ is the standard t-value. Solving for x(y=0) using the quadratic equation for $0 = ax^2 + bx + c$, we have

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a},$$

with

$$a = \frac{B^2}{t^2 \cdot \text{MSE}} - \frac{1}{n-1}$$
$$b = \frac{2AB}{t^2 \cdot \text{MSE}} + \frac{2\overline{x}}{n-1}$$
$$c = \frac{A^2}{t^2 \cdot \text{MSE}} - 1 - \frac{1}{n} - \frac{\overline{x}^2}{n-1}$$

Although this method for the calculation of uncertainty in the threshold energy is valid, it should be noted that the least squares fitting procedure assumes that the energy values are precisely controlled and have negligible error. Since the errors on the x-axis $(\ln(E))$ are of comparable magnitude to those on the y-axis (D^2) , this assumption is not true. Therefore, the parameters determined by this method may be slightly biased by this neglect. To offset this, the uncertainty in the x values is added directly to the calculated uncertainty of the threshold energy. The uncertainty for each threshold becomes $\sigma + 0.03$. It is hoped that this will overestimate the uncertainty in this term and account for any bias introduced into the slope, B, when calculating the threshold fluences for each number of pulses. Pre-pulses and postpulses are inherent in the regeneratively amplified ultrafast laser system and are potentially another source of error. Post pulses are typically < 2% of the total energy, while pre-pulses are generally < 0.1% of the total energy (in one case the pre-pulse energy was higher than normal, at 0.4%). This means that the quantity of energy in a given pulse may be overestimated by a couple percent. On the other hand, the post pulse may interact with a softened surface, which is more susceptible to damage, therefore having the reverse effect. However, for experiments done at $\lambda = 400$ nm, the weaker pulses will be inefficiently converted and their contribution to the total energy is considered negligible.

The threshold fluences for each number of pulses are all calculated using the slope of the single shot data for consistency. The laser spot size should not change significantly during an experimental run and so any variation in the slopes for different numbers of pulses is due to measurement error, non-locality of energy deposition or other effects. The uncertainty in the threshold fluence is calculated by error propagation using the known uncertainties in the threshold energy and single shot spot size.

There is a larger amount of variation in the calculated slopes (and therefore spot sizes) than the uncertainty alone can account for. Consider for example, the case at $\lambda = 400$ nm. Although the uncertainty in each of the individual slopes for each number of pulses is at a maximum 0.15 μ m, the standard deviation of the slopes of each set of data is 0.5 μ m. The different slopes extracted from each set of data seems to be a real phenomenon (that is, not simply a result of random errors). Possible explanations for this are a time-varying energy, real changes in the size of the collimated beam diameter out of the laser system, beam pointing stability, and pulse number-dependent non-locality of energy deposition.

A time varying pulse energy could lead to varied slopes but should also cause a breakdown in linearity. This may not be easily observed since it may be lost in the scatter of the data. Real changes in the collimated beam diameter must be on the order of 8 percent to achieve the observed changes in spot size. Measurements of this diameter over a several hour period would be helpful for quantifying the actual stability.

Non-locality of energy deposition is another consideration. For one, heated material may flow, leading to a wider distribution of energy than that delivered by the incident beam. The mean distance of material flow is not expected to depend on the size of the incident spot, so presumably the use of larger spot sizes could mitigate this effect. Also, lateral scattering of sub-threshold incident radiation due to a rippled surface may distribute the incident energy in a wider region than the nominal spot size. The sub-threshold radiation may lead to ablation in subsequent pulses due to the incubation effect.

A limitation on the incubation effect as the number of pulses approaches infinity has been alluded to by some authors, in particular in [33]. It is not physically reasonable to expect that a surface can be damaged by vanishingly small pulse energies by sufficiently increasing the number of incident pulses. However, it is important to consider at which point the incubation effect saturates (that is, the pulse energy at which no amount of further irradiation will cause damage or ablation). There is some evidence that this point may be lower than a factor of five below the single pulse threshold for CaF_2 [46].

An alternative method (to the D^2 method) for determining thresholds would be to claim that the threshold pulse energy lies between the pulse energy for the last observed crater and that for the case in which a crater is not formed. This method is impervious to the assumptions of locality and Gaussian profile but requires very fine control of the pulse energy and enough material to perform the multiple experimental runs required obtain a resolution superior to the D^2 method.

Chapter 5

Conclusion

The creation of ordered ripples on surfaces following laser irradiation has been observed since 1965. These structures have received substantial attention for both scientific and technological interest. In this thesis, the characterization of surface ripples on single crystal diamond by femtosecond laser pulse irradiation is reported. Ripples are created by direct surface irradiation at normal and varying angles of incidence. The beam is either stationary or translated across the surface. Also, a rough surface is irradiated at grazing incidence after propagating the beam through substantial amounts of bulk material. Two wavelengths of incident femtosecond pulses are explored in addition to a broad range of fluences and number of pulses.

A strong propensity for ripples to form is found for irradiation with ultrashort 800 nm pulses from above the multi-shot ablation threshold up to at least one order of magnitude above the ablation threshold. Generally, for surface irradiation, two types of ripples form. One type with periodicity somewhat below the incident wavelength, λ , and one type with periodicity close to the $\lambda/2n$. A variety of morphologies can be observed, which may be indicative of the mechanisms of formation, ranging to periodic smooth wavelike structures to ordered nanocracks penetrating deep into the material. The orientation and morphology of ripples are found to be strongly dependent on laser polarization, with ripples aligning perpendicular to the polarization in nearly every situation, while circular polarization leads to the formation of nano-sized circular structures. The angle of incidence is found to affect the propensity for HSFL formation for p-polarized irradiation. In addition, the ripples periodicity of LSFL structures is found to be strongly dependent on the angle of incidence.

Propagating ultrashort pulses through bulk material has led to new outcomes not previously observed in diamond, although there is still the question of whether the surface remains crystalline. The periodicity is substantially reduced to 50 nm in one case and routinely below 70 nm with altered morphology characterized by many bifurcations and regional misorientation. It is likely that the misorientation is due to strain-induced birefringence within the diamond bulk.

Ripple periodicity can be controlled through selection of appropriate parameters including fluence and numbers of pulses. In addition, angle of incidence and irradiation of a back or side surface can offer further control of ripple periodicity to tune ultra fine structuring substantially below the irradiation wavelength.

Existing models in the literature are closely followed by ripple periodicity trends, particularly for the case of LSFL periodicity as a function of angle of incidence, which is a strong indicator that the classical models provide sufficient explanation for the parameter space explored here. The mechanisms of HSFL formation are still under discussion in the literature, although certain outcomes may be more supportive of the nanoplasmonics models. In general, both classical and self assembly models offer plausible explanations for their formation. In addition, ablation thresholds for single and multiple femtosecond pulse irradiation of a single crystal diamond surface are analyzed and incubation properties are reported.

The single femtosecond pulse ablation threshold at 800 nm was found to be 2.3 J/cm², while at 400 nm the threshold is reduced to 1.5 J/cm². This result is in general agreement with other reports. Diamond was found to exhibit strong incubation behaviour at both wavelengths with only a slight difference in the incubation coefficient, unless a baseline is introduced in which case the material incubates more strongly with 800 nm pulses. Power law models are were found to be an incomplete description of incubation behaviour. Similarly, exponential laws failed to correctly model incubation behaviour at both wavelengths in diamond. This could be indicative of a complex mechanism or combination of mechanisms being involved in the memory effect of past pulses. The error in determining the ablation threshold for these experiments is generally the range of 15 - 20% but could be improved somewhat by using larger pulse diameters.

On the ripples front, future work might include repeating experimental efforts to determine an angular dependence for s-polarized light, which could further progress our understanding where diamond irradiated with ultrashort pulses fits into the Sipe picture or other models. Work with the optical parametric amplifier (OPA) can be resumed to extend the line of investigation on the wavelength dependence.

To solidify the results already obtained, an efficient method for collecting data on both incubation and ripples studies is to perform arrays of single and multiple pulse irradiation at varying pulse energies. The appropriate parameter space can be chosen through current knowledge of thresholds and simulations. Improvements over past experiments in terms of spot size (larger) and material quality will also be made.

There are some interesting ripples examples to consider for focused ion beamtransmission electron microscopy (FIB-TEM) analysis to reveal detailed ripple morphology and crystallinity. First, scanning many shots across a double side polished back surface indicates in some cases the formation on nanoplane-like structures, the depth of which could be confirmed by FIB-TEM perhaps combined with an etching procedure such as used in [25]. Second, the fine ripples created by irradiation at angles of incidence exceeding 45° exhibit a unique appearance on the surface, which may provide a new avenue of insight into mechanisms if investigated cross sectionally. Third, ultra fine ripples observed after substantial processing might be investigated to reveal the material crystallinity. Ripples of similar periodicity have been observed in an amorphous carbon coating on diamond [75], but this would mark the first observation of such periodicity in crystalline diamond provided the material composition can be verified.

To follow up with the ripples created after propagation through bulk material, one can focus a beam onto the back edge of varying qualities of diamond using a high NA objective to see whether the misorientation of the ripples is due to intrinsic material properties or an interaction in the material.

Imperfect sample quality might be grounds for calling some results into question. With new high quality samples, one can perform clean incubation and ripples experiments in the manner described above. New samples have already been obtained, containing lower impurity levels and improved surface polishing (free of pitting). The formation of a thin amorphous film should be investigated further as well through the utilization of surface measurement techniques such as surface enhanced Raman scattering (SERS).

The available facilities at McMaster extend the possible scientific aims to new work involving the manipulation of the nitrogen vacancy complex in diamond. This is a significant area of research receiving substantial attention in recent years [95–107] which may have some relation to the present work. The search to find applications of ultrafast lasers in quantum computing has so far been successful, largely due to time resolution in manipulating single spins carried by the Nitrogen centres. In addition, ultrafast lasers may be able to speed material preparation. Currently, diamond is prepared with nitrogen substitutions and single vacancies and annealed at 700 °C for a specified time to allow the vacancies to become mobile. The nitrogen substitutions act as a sink for vacancies, which become trapped, yielding a (usually negatively charged) nitrogen vacancy complex [96]. The process for creating the vacancies typically involves ion or electron beam irradiation and a series of ultrashort laser pulses may be applicable to larger areas simultaneously or used in nanopatterning along the same lines as ripples. Since incubation is a long-lived phenomenon, some researchers working on silicon consider the possibility that the physical manifestation of incubation is the creation of single vacancies, which combine to form di-vacancies (stable at room temperature). If similar laser-material interaction (and in particular, incubation) mechanisms are involved for diamond and silicon, then it is possible that vacancies might be generated in diamond as well. From this line of reasoning, it may be possible to selectively create vacancies in bulk or near the surface using ultrafast laser pulses to position nitrogen vacancies in diamond. This would provide an alternative process compared to ion or electron beams and offers greater flexibility because of the prospect of positioning vacancies deep in the bulk.

Appendix A

Contributions

Femtosecond laser interactions with diamond, silicon, and ion-implanted silicon. J.A.Z.Brawley-Hayes, E.M. Hsu, H.K. Haugen, P.E. Jessop, A.P. Knights, and T. Jacob.FemtoMat Nano and Photonics Conference. Austria, 2011.

Femtosecond laser based modification and damage thresholds of synthetic single crystal diamond. J.A.Z. Brawley-Hayes, E.M. Hsu, H.K. Haugen. **Conference on Laser Ablation.** Mexico, 2011.

Bibliography

- T. H. Maiman, "Stimulated optical radiation in ruby," *Nature*, vol. 187, no. 4736, pp. 493–494, 1960.
- [2] P. W. Milonni and J. H. Eberly, *Lasers*. United States of America: John Wiley and Sons, Inc., 1988.
- [3] L. E. Hargrove, R. L. Fork, and M. A. Pollack, "Locking of He-Ne laser modes induced by synchronous intracavity modulation," *Applied Physics Letters*, vol. 5, pp. 4–5, 1964.
- [4] E. Lerner, "Industrial laser cutting goes mainstream," Laser Focus World, vol. 35, no. 6, pp. 113–114, 1999.
- [5] G. Ogura, J. Angell, and D. Wall, "Applications test potential of laser micromachining," *Laser Focus World*, vol. 34, no. 6, pp. 117–118, 1998.
- [6] D. Bauerle, Laser Processing and Chemistry. Berlin, Germany: Springer, 2000.
- [7] M. D. Perry, B. C. Stuart, P. S. Banks, M. D. Feit, V. Yanovsky, and A. M. Rubenchik, "Ultrashort-pulse laser machining of dielectric materials," *Journal of Applied Physics*, vol. 85, no. 9, pp. 6803–6810, 1999.

- [8] M. Feit, A. Komashko, and A. Rubenchik, "Ultra-short pulse laser interaction with transparent dielectrics," *Applied Physics A*, vol. A79, no. 7, pp. 1657–1661, 2004.
- [9] S. Adachi, Optical constants of crystalline and amorphous semiconductors. Kluwer Academic Publishers, 1999.
- [10] Y. Gurbuz, O. Esame, I. Tekin, W. Kang, and J. Davidson, "Diamond semiconductor technology for RF device applications," *Solid-State Electronics*, vol. 49, no. 7, pp. 1055–1070, 2005.
- [11] I. Friel, S. Clewes, H. Dhillon, N. Perkins, D. Twitchen, and G. Scarsbrook, "Control of surface and bulk crystalline quality in single crystal diamond grown by chemical vapour deposition," *Diamond and Related Materials*, vol. 18, no. 5-8, pp. 808–815, 2009.
- [12] E. Hsu, N. Mailman, G. Botton, and H. Haugen, "Microscopic investigation of single-crystal diamond following ultrafast laser irradiation," *Applied Physics A*, vol. 103, no. 1, pp. 185–192, 2011.
- [13] R. Takalkar, J. Davidson, W. Kang, A. Wisitsora-at, and D. Kerns, "Edgeshaped diamond field emission arrays," *Journal of Vacuum Science & Technol*ogy B, vol. 23, no. 2, pp. 800–804, 2005.
- [14] T. M. Babinec, B. J. M. Hausmann, M. Khan, Y. Zhang, J. R. Maze, P. R. Hemmer, and M. Loncar, "A diamond nanowire single-photon source," *Nature Nanotechnology*, vol. 5, pp. 195–199, 2010.

- [15] H. van Driel, J. Sipe, and J. Young, "Laser-induced periodic surface structure on solids: A universal phenomenon," *Physical Review Letters*, vol. 49, no. 26, pp. 1955–1958, 1982.
- [16] J. Reif, F. Costache, M. Henyk, and S. V. Pandelov, "Ripples revisited: Nonclassical morphology at the bottom of femtosecond laser ablation craters in transparent dielectrics," *Applied Surface Science*, vol. 197-198, pp. 891–895, 2002.
- [17] M. Huang, F. Zhao, Y. Cheng, N. Xu, and Z. Xu, "Origin of laser-induced near-subwavelength ripples: Interference between surface plasmons and incident laser," ACS Nano, vol. 3, no. 12, pp. 4062–4070, 2009.
- [18] M. Huang, F. Zhao, Y. Cheng, N. Xu, and Z. Xu, "Mechanisms of ultrafast laser-induced deep-subwavelength gratings on graphite and diamond," *Physical Review B*, vol. 79, no. 12, p. 125436, 2009.
- [19] T. Jia, H. Chen, M. Huang, F. Zhao, J. Qiu, R. Li, Z. Xu, X. He, J. Zhang, and H. Kuroda, "Formation of nanogratings on the surface of a znse crystal irradiated by femtosecond laser pulses," *Physical Review B*, vol. 72, no. 12, p. 125429, 2005.
- [20] J. Reif, O. Varlamova, and F. Costache, "Femtosecond laser induced nanostructure formation: Self-organization control parameters," *Applied Physics A*, vol. 92, no. 4, pp. 1019–1024, 2008.
- [21] D. Dufft, A. Rosenfeld, S. K. Das, R. Grunwald, and J. Bonse, "Femtosecond

laser-induced periodic surface structures revisited: A comparative study on ZnO," *Journal of Applied Physics*, vol. 105, no. 3, p. 034908, 2009.

- [22] J. Bonse, M. Munz, and H. Sturm, "Structure formation on the surface of indium phosphide irradiated by femtosecond laser pulses," *Journal of Applied Physics*, vol. 97, no. 1, p. 13538, 2005.
- [23] J. Bonse, A. Rosenfeld, and J. Kruger, "Implications of transient changes of optical and surface properties of solids during femtosecond laser pulse irradiation to the formation of laser-induced periodic surface structures," *Applied Surface Science*, vol. 257, pp. 5420–5423, 2011.
- [24] V. R. Bhardwaj, E. Simova, P. P. Rajeev, C. Hnatovsky, R. S. Taylor, D. M. Rayner, and P. B. Corkum, "Optically produced arrays of planar nanostructures inside fused silica," *Physical Review Letters*, vol. 96, no. 5, p. 057404, 2006.
- [25] M. Shinoda, R. R. Gattass, and E. Mazur, "Femtosecond laser-induced formation of nanometer-width grooves on synthetic single-crystal diamond surfaces," *Journal of Applied Physics*, vol. 105, no. 5, p. 053102, 2009.
- [26] J. E. Sipe, J. F. Young, J. S. Preston, and H. M. van Driel, "Laser-induced periodic surface structure. I. Theory," *Physical Review B*, vol. 27, no. 2, pp. 1141– 1154, 1983.
- [27] J. Young, J. Preston, H. van Driel, and J. Sipe, "Laser-induced periodic surface structure. II. Experiments on Ge, Si, Al, and brass," *Physical Review B*, vol. 27, no. 2, pp. 1155–1172, 1983.

- [28] A. Borowiec, M. Mackenzie, G. Weatherly, and H. Haugen, "Femtosecond laser pulse ablation of GaAs and InP: Studies utilizing scanning and transmission electron microscopy," *Applied Physics A*, vol. A77, no. 3-4, pp. 411–417, 2003.
- [29] A. Borowiec, H. Tiedje, and H. Haugen, "Wavelength dependence of the single pulse femtosecond laser ablation threshold of indium phosphide in the 400-2050 nm range," *Applied Surface Science*, vol. 243, no. 1-4, pp. 131–139, 2005.
- [30] T. Crawford, A. Borowiec, and H. Haugen, "Femtosecond laser micromachining of grooves in silicon with 800 nm pulses," *Applied Physics A*, vol. A80, no. 8, pp. 1717–1724, 2005.
- [31] R. Sussmann, G. Scarsbrook, C. Wort, and R. Wood, "Laser damage testing of CVD-grown diamond windows," *Diamond and Related Materials*, vol. 3, no. 9, pp. 1173–1177, 1994.
- [32] D. J. Spence, E. Granados, and R. P. Mildren, "Mode-locked picosecond diamond raman laser," *Optics Letters*, vol. 35, no. 4, pp. 556–558, 2010.
- [33] D. Ashkenasi, M. Lorenz, R. Stoian, and A. Rosenfeld, "Surface damage threshold and structuring of dielectrics using femtosecond laser pulses: The role of incubation," *Applied Surface Science*, vol. 150, no. 1, pp. 101–106, 1999.
- [34] L. Qi, K. Nishii, M. Yasui, H. Aoki, and Y. Namba, "Femtosecond laser ablation of sapphire on different crystallographic facet planes by single and multiple laser pulses irradiation," *Optics and Lasers in Engineering*, vol. 48, no. 10, pp. 1000– 1007, 2010.

- [35] L. V. Keldysh, "Ionization in the field of a strong electromagnetic wave," Soviet Physics JETP, vol. 20, no. 5, pp. 1307–1314, 1965.
- [36] Y. Shimotsuma, P. G. Kazansky, J. Qiu, and K. Hirao, "Self-organized nanogratings in glass irradiated by ultrashort light pulses," *Physical Review Letters*, vol. 91, no. 24, p. 247405, 2003.
- [37] B. H. Christensen and P. Balling, "Modeling ultrashort-pulse laser ablation of dielectric materials," *Physical Review B*, vol. 79, no. 15, p. 155424, 2009.
- [38] C. Schaffer, A. Brodeur, and E. Mazur, "Laser-induced breakdown and damage in bulk transparent materials induced by tightly focused femtosecond laser pulses," *Measurement Science and Technology*, vol. 12, no. 11, pp. 1784–1794, 2001.
- [39] B. C. Stuart, M. D. Felt, S. Herman, and A. M. Rubenchik, "Nanosecond-tofemtosecond laser-induced breakdown in dielectrics," *Physical Review B*, vol. 53, no. 4, pp. 1749–1749, 1996.
- [40] R. R. Gattass and E. Mazur, "Femtosecond laser micromachining in transparent materials," *Nature Photonics*, vol. 2, no. 4, pp. 219–225, 2008.
- [41] D. Puerto, W. Gawelda, J. Siegel, J. Bonse, G. Bachelier, and J. Solis, "Transient reflectivity and transmission changes during plasma formation and ablation in fused silica induced by femtosecond laser pulses," *Applied Physics A*, vol. 92, no. 4, pp. 803–808, 2008.

- [42] D. von der Linde, K. Sokolowski-Tinten, and J. Bialkowski, "Laser-solid interaction in the femtosecond time regime," *Applied Surface Science*, vol. 109-110, pp. 1–10, 1997.
- [43] L. J. Lewis and D. Perez, "Laser ablation with short and ultrashort laser pulses: Basic mechanisms from molecular-dynamics simulations," *Applied Surface Science*, vol. 255, no. 10, pp. 5101–5106, 2009.
- [44] D. Perez and L. J. Lewis, "Molecular-dynamics study of ablation of solids under femtosecond laser pulses," *Physical Review B*, vol. 67, no. 18, p. 184102, 2003.
- [45] D. Ashkenasi, R. Stoian, and A. Rosenfeld, "Single and multiple ultrashort laser pulse ablation threshold of Al₂O₃ (corundum) at different etch phases," *Applied Surface Science*, vol. 154-155, pp. 40–46, 2000.
- [46] F. Costache and J. Reif, "Femtosecond laser induced coulomb explosion from calcium fluoride," *Thin Solid Films*, vol. 453-454, pp. 334–339, 2004.
- [47] W. Roeterdink, L. Juurlink, O. Vaughan, J. Dura Diez, M. Bonn, and A. Kleyn,
 "Coulomb explosion in femtosecond laser ablation of Si(111)," *Applied Physics Letters*, vol. 82, no. 23, pp. 4190–4192, 2003.
- [48] R. Stoian, D. Ashkenasi, A. Rosenfeld, and E. Campbell, "Coulomb explosion in ultrashort pulsed laser ablation of Al₂O₃," *Physical Review B*, vol. 62, no. 19, pp. 13167–13173, 2000.
- [49] N. Bulgakova, R. Stoian, A. Rosenfeld, I. Hertel, W. Marine, and E. Campbell,"A general continuum approach to describe fast electronic transport in pulsed

laser irradiated materials: the problem of coulomb explosion," *Applied Physics* A, vol. A81, no. 2, pp. 345–356, 2005.

- [50] H. Dachraoui, W. Husinsky, and G. Betz, "Ultra-short laser ablation of metals and semiconductors: Evidence of ultra-fast coulomb explosion," *Applied Physics* A, vol. A83, no. 2, pp. 333–336, 2006.
- [51] M. Birnbaum, "Semiconductor surface damage produced by ruby lasers," Journal of Applied Physics, vol. 36, pp. 3688–3690, 1965.
- [52] J. Bonse and J. Kruger, "Pulse number dependence of laser-induced periodic surface structures for femtosecond laser irradiation of silicon," *Journal of Applied Physics*, vol. 108, no. 3, p. 034903, 2010.
- [53] A. Borowiec and H. Haugen, "Subwavelength ripple formation on the surfaces of compound semiconductors irradiated with femtosecond laser pulses," *Applied Physics Letters*, vol. 82, no. 25, pp. 4462–4464, 2003.
- [54] G. Obara, Y. Tanaka, N. Nedyalkov, M. Terakawa, and M. Obara, "Direct observation of surface plasmon far field for regular surface ripple formation by femtosecond laser pulse irradiation of gold nanostructures on silicon substrates," *Applied Physics Letters*, vol. 99, no. 6, p. 061106, 2011.
- [55] W. Ding, R. Bachelot, S. Kostcheev, P. Royer, and R. Espiau de Lamaestre, "Surface plasmon resonances in silver bowtie nanoantennas with varied bow angles," *Journal of Applied Physics*, vol. 108, no. 12, p. 124314, 2010.
- [56] E. Hsu, T. Crawford, H. Tiedje, and H. Haugen, "Periodic surface structures

on gallium phosphide after irradiation with 150 fs-7 ns laser pulses at 800 nm," Applied Physics Letters, vol. 91, no. 11, p. 111102, 2007.

- [57] E. Hsu, T. Crawford, C. Maunders, G. Botton, and H. Haugen, "Cross-sectional study of periodic surface structures on gallium phosphide induced by ultrashort laser pulse irradiation," *Applied Physics Letters*, vol. 92, no. 22, p. 221112, 2008.
- [58] P. P. Rajeev, M. Gertsvolf, C. Hnatovsky, E. Simova, R. S. Taylor, P. B. Corkum, D. M. Rayner, and V. R. Bhardwaj, "Transient nanoplasmonics inside dielectrics," *Journal of Physics B*, vol. 40, no. 11, pp. S273–S282, 2007.
- [59] G. Boyd, T. Rasing, J. Leite, and Y. Shen, "Local-field enhancement on rough surfaces of metals, semimetals, and semiconductors with the use of optical second-harmonic generation," *Physical Review B*, vol. 30, no. 2, pp. 519–526, 1984.
- [60] O. Varlamova, F. Costache, M. Ratzke, and J. Reif, "Control parameters in pattern formation upon femtosecond laser ablation," *Applied Surface Science*, vol. 253, no. 19, pp. 7932–7936, 2007.
- [61] F. Costache, M. Henyk, and J. Reif, "Modification of dielectric surfaces with ultra-short laser pulses," *Applied Surface Science*, vol. 186, pp. 352–357, 2002.
- [62] J. Reif, O. Varlamova, M. Ratzke, M. Schade, H. Leipner, and T. Arguirov, "Multipulse feedback in self-organized ripples formation upon femtosecond laser ablation from silicon," *Applied Physics A*, vol. 101, no. 2, pp. 361–365, 2010.
- [63] R. Cuerno and A.-L. Barabasi, "Dynamic scaling of ion-sputtered surfaces," *Physical Review Letters*, vol. 74, no. 23, pp. 4746–4746, 1995.

- [64] J. Reif, O. Varlamova, F. Costache, and M. Bestehorn, "Self-organized pattern formation upon femtosecond laser ablation by circularly polarized light," *Applied Surface Science*, vol. 252, no. 13, pp. 4702–4706, 2006.
- [65] O. Varlamova, J. Reif, S. Varlamov, and M. Bestehorn, "The laser polarization as control parameter in the formation of laser-induced periodic surface structures: Comparison of numerical and experimental results," *Applied Surface Science*, vol. 257, no. 12, pp. 5465–5469, 2011.
- [66] Y. Jee, M. Becker, and R. Walser, "Laser-induced damage on single-crystal metal surfaces," *Journal of the Optical Society of America B*, vol. 5, no. 3, pp. 648–659, 1988.
- [67] S. Beke, K. Sugioka, K. Midorikawa, A. Peter, L. Nanai, and J. Bonse, "Characterization of the ablation of TeO₂ crystals in air with femtosecond laser pulses," *Journal of Physics D*, vol. 43, no. 2, p. 025401, 2010.
- [68] R. W. Boyd, Nonlinear Optics. San Diego, CA: Academic Press, 2003.
- [69] J.-Y. Zhang, J. Huang, H. Wang, K. Wong, and G. Wong, "Second-harmonic generation from regeneratively amplified femtosecond laser pulses in BBO and LBO crystals," *Journal of the Optical Society of America B*, vol. 15, no. 1, pp. 200–209, 1998.
- [70] N. Bloembergen, "Role of cracks, pores, and absorbing inclusions on laser induced damage threshold at surfaces of transparent dielectrics," *Applied Optics*, vol. 12, no. 4, pp. 661–664, 1973.

- [71] D. Fedoseev, S. Vnukov, V. Bukhovets, and B. Anikin, "Surface graphitization of diamond at high temperatures," *Surface and Coatings Technology*, vol. 28, no. 2, pp. 207–214, 1986.
- [72] J. Kruger, D. Dufft, R. Koter, and A. Hertwig, "Femtosecond laser-induced damage of gold films," *Applied Surface Science*, vol. 253, no. 19, pp. 7815–7819, 2007.
- [73] S. Das, K. Dasari, A. Rosenfeld, and R. Grunwald, "Extended-area nanostructuring of TiO₂ with femtosecond laser pulses at 400 nm using a line focus," *Nanotechnology*, vol. 21, no. 15, p. 155302, 2010.
- [74] V. Mitko, G. Roer, A. Huis in't Veld, J. Skolski, J. Obona, V. Ocelik, and J. De Hosson, "Properties of high-frequency sub-wavelength ripples on stainless steel 304L under ultra short pulse laser irradiation," *Physics Procedia*, vol. 12, pp. 99–104, 2011.
- [75] M. Forster, Physico-chemical modification and ablation of solid materials by ultrashort laser pulses. Dissertation, Universitat Wien, 2010.
- [76] Q. Zhao, F. Ciobanu, S. Malzer, and L. Wang, "Enhancement of optical absorption and photocurrent of 6H-SiC by laser surface nanostructuring," *Applied Physics Letters*, vol. 91, no. 12, p. 121107, 2007.
- [77] D. Puerto, W. Gawelda, J. Siegel, J. Solis, and J. Bonse, "Erratum: "plasma formation and structural modification below the visible ablation threshold in fused silica upon femtosecond laser irradiation" [applied physics letters (2007) 91 (082902)]," Applied Physics Letters, vol. 92, no. 21, p. 219901, 2008.

- [78] J. Siegel, D. Puerto, W. Gawelda, G. Bachelier, J. Solis, L. Ehrentraut, and J. Bonse, "Plasma formation and structural modification below the visible ablation threshold in fused silica upon femtosecond laser irradiation," *Applied Physics Letters*, vol. 91, no. 8, p. 082902, 2007.
- [79] D. Ashkenasi, G. Muller, A. Rosenfeld, R. Stoian, I. V. Hertel, N. M. Bulgakova, and E. E. B. Campbell, "Fundamentals and advantages of ultrafast micro-structuring of transparent materials," *Applied Physics A*, vol. A77, no. 2, pp. 223–228, 2003.
- [80] K. Okamuro, M. Hashida, Y. Miyasaka, Y. Ikuta, S. Tokita, and S. Sakabe, "Laser fluence dependence of periodic grating structures formed on metal surfaces under femtosecond laser pulse irradiation," *Physical Review B*, vol. 82, no. 16, p. 165417, 2010.
- [81] J. Byskov-Nielsen, J.-M. Savolainen, M. S. Christensen, and P. Balling, "Ultrashort pulse laser ablation of metals: Threshold fluence, incubation coefficient and ablation rates," *Applied Physics A*, vol. 101, no. 1, pp. 97–101, 2010.
- [82] P. Mannion, J. Magee, E. Coyne, G. O'Connor, and T. Glynn, "The effect of damage accumulation behaviour on ablation thresholds and damage morphology in ultrafast laser micro-machining of common metals in air," *Applied Surface Science*, vol. 233, no. 1-4, pp. 275–287, 2004.
- [83] A. M. Ozkan, A. P. Malshe, T. A. Railkar, W. D. Brown, M. D. Shirk, and P. A. Molian, "Femtosecond laser-induced periodic structure writing on diamond crystals and microclusters," *Applied Physics Letters*, vol. 75, no. 23, pp. 3716–3718, 1999.

- [84] G. Dumitru, V. Romano, H. Weber, M. Sentis, and W. Marine, "Femtosecond ablation of ultrahard materials," *Applied Physics A*, vol. A74, no. 6, pp. 729– 739, 2002.
- [85] G. Miyaji and K. Miyazaki, "Origin of periodicity in nanostructuring on thin film surfaces ablated with femtosecond laser pulses," *Optics Express*, vol. 16, no. 20, pp. 16265–16271, 2008.
- [86] M. Rohloff, S. Das, S. Hohm, R. Grunwald, A. Rosenfeld, J. Kruger, and J. Bonse, "Formation of laser-induced periodic surface structures on fused silica upon multiple cross-polarized double-femtosecond-laser-pulse irradiation sequences," *Journal of Applied Physics*, vol. 110, no. 1, p. 014910, 2011.
- [87] X. Wang, G. Lim, F. Ng, W. Liu, and S. Chua, "Femtosecond pulsed laserinduced periodic surface structures on GaN/sapphire," *Applied Surface Science*, vol. 252, no. 5, pp. 1492–1497, 2005.
- [88] X. Guo, R. Li, Y. Hang, Z. Xu, B. Yu, H. Ma, B. Lu, and X. Sun, "Femtosecond laser-induced periodic surface structure on ZnO," *Materials Letters*, vol. 62, no. 12-13, pp. 1769 – 1771, 2008.
- [89] G. Seifret, M. Kaempfe, F. Syrowatka, C. Harnagea, D. Hesse, and H. Graener, "Self-organized structure formation on the bottom of femtosecond laser ablation craters in glass," *Applied Physics A*, vol. A81, no. 4, pp. 799–803, 2005.
- [90] Q. Wu, Y. Ma, R. Fang, Y. Liao, Q. Yu, X. Chen, and K. Wang, "Femtosecond laser-induced periodic surface structure on diamond film," *Applied Physics Letters*, vol. 82, no. 11, pp. 1703–1705, 2003.
- [91] T. Y. Hwang and C. Guo, "Angular effects of nanostructure-covered femtosecond laser induced periodic surface structures on metals," *Journal of Applied Physics*, vol. 108, no. 7, p. 073523, 2010.
- [92] J. Mossbrucker and T. Grotjohn, "Determination of local crystal orientation of diamond using polarized raman spectra," *Diamond and Related Materials*, vol. 5, no. 11, pp. 1333–1343, 1996.
- [93] S. Mao, F. Quere, S. Guizard, X. Mao, R. Russo, G. Petite, and P. Martin, "Dynamics of femtosecond laser interactions with dielectrics," *Applied Physics A*, vol. A79, no. 7, pp. 1695–1709, 2004.
- [94] N. Bloembergen, "Surface nonlinear optics: a historical overview," Applied Physics B, vol. B68, no. 3, pp. 289–293, 1999.
- [95] Y. Chi, G. Chen, F. Jelezko, E. Wu, and H. Zeng, "Enhanced photoluminescence of single-photon emitters in nanodiamonds on a gold film," *IEEE Photonics Technology Letters*, vol. 23, no. 6, pp. 374–376, 2011.
- [96] S. Pezzagna, D. Rogalla, D. Wildanger, J. Meijer, and A. Zaitsev, "Creation and nature of optical centres in diamond for single-photon emission - overview and critical remarks," *New Journal of Physics*, vol. 13, no. 3, p. 035024, 2011.
- [97] Y. Dumeige, R. Alleaume, P. Grangier, F. Treussart, and J. F. Roch, "Controling the single-diamond nitrogen-vacancy color center photoluminescence spectrum with a fabry-perot microcavity," *New Journal of Physics*, vol. 13, no. 2, p. 025015, 2011.

- [98] O. E. Mustecaplioglu, "Quantum coherence and correlations of optical radiation by atomic ensembles interacting with a two-level atom in a microwave cavity," *Physical Review A*, vol. 83, no. 2, p. 023805, 2011.
- [99] T. M. Babinec, J. T. Choy, K. J. M. Smith, M. Khan, and M. Loncar, "Design and focused ion beam fabrication of single crystal diamond nanobeam cavities," *Journal of Vacuum Science & Technology B*, vol. 29, no. 1, p. 010601, 2011.
- [100] P. Spinicelli, A. Dreau, L. Rondin, F. Silva, J. Achard, S. Xavier, S. Bansropun, T. Debuisschert, S. Pezzagna, J. Meijer, V. Jacques, and J. F. Roch, "Engineered arrays of nitrogen-vacancy color centers in diamond based on implantation of cn- molecules through nanoapertures," *New Journal of Physics*, vol. 13, no. 2, p. 025014, 2011.
- [101] J. R. Maze, A. Gali, E. Togan, Y. Chu, A. Trifonov, E. Kaxiras, and M. D. Lukin, "Properties of nitrogen-vacancy centers in diamond: the group theoretic approach," *New Journal of Physics*, vol. 13, no. 2, p. 025025, 2011.
- [102] A. Gali, T. Simon, and J. E. Lowther, "An ab initio study of local vibration modes of the nitrogen-vacancy center in diamond," New Journal of Physics, vol. 13, no. 2, p. 025016, 2011.
- [103] N. Zhao, J.-L. Hu, S.-W. Ho, J. K. Wan, and R. B. Liu, "Atomic-scale magnetometry of distant nuclear spin clusters via nitrogen-vacancy spin in diamond," *Nature Nanotechnology*, vol. 6, no. 4, pp. 242–246, 2011.
- [104] R. Hanson, O. Gywat, and D. D. Awschalom, "Room-temperature manipulation

and decoherence of a single spin in diamond," *Physical Review B*, vol. 74, no. 16, p. 161203, 2006.

- [105] B. J. Maertz, A. P. Wijnheijmer, G. D. Fuchs, M. E. Nowakowski, and D. D. Awschalom, "Vector magnetic field microscopy using nitrogen vacancy centers in diamond," *Applied Physics Letters*, vol. 96, no. 9, p. 092504, 2010.
- [106] L. Childress, M. V. G. Dutt, J. M. Taylor, A. S. Zibrov, F. Jelezko, J. Wrachtrup, P. R. Hemmer, and M. D. Lukin, "Coherent dynamics of coupled electron and nuclear spin qubits in diamond," *Science*, vol. 314, no. 5797, pp. 281–285, 2006.
- [107] R. Hanson, F. M. Mendoza, R. J. Epstein, and D. D. Awschalom, "Polarization and readout of coupled single spins in diamond," *Physical Review Letters*, vol. 97, no. 8, p. 087601, 2006.