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ABLATION AND MICROMACHINING OF INP WITH FEMTOSECOND LASER PULSES

By

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A Thesis

**Submitted to the School of Graduate Studies
In Partial Fulfillment of the Requirements
for the Degree
Doctor of Philosophy**

McMaster University

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**ABLATION AND MICROMACHINING
OF INP WITH FEMTOSECOND LASER
PULSES**

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Abstract

This thesis details the results of femtosecond laser ablation and micromachining of indium phosphide (InP). The experimental results presented consist of six sets of investigations divided into two categories: 1) single and multiple pulse ablation of stationary samples; 2) laser micromachining and analysis of grooves cut in InP.

The first series of experiments dealt with the analysis of the final state of InP after single and multiple pulse irradiation. The experiments were performed with femtosecond pulses, 60 – 175 fs in duration, centered around wavelengths of 400, 800, 660, 800, 1300 and 2100 nm.

In the first set of investigations, single pulse laser ablation craters on InP and GaAs were studied via scanning and plan-view transmission electron microscopy. The final state of the material near the laser-ablated region following femtosecond ablation was characterized in detail for three selected laser fluences.

In the second set of investigations, single pulse ablation threshold measurements were performed in the wavelength range from 400 – 2100 nm, covering the photon energy above and below the bandgap of InP. The ablation thresholds determined from depth and volume measurements varied from 87 mJ/cm² at 400 nm to 250 mJ/cm² at 2050 nm. The measurements were performed with optical microscopy, atomic force and scanning electron microscopy. In addition, sharp onsets of the measured depths versus laser fluence were observed at the ablation thresholds.

In the third set of investigations, laser induced periodic surface structures were investigated on the surfaces of InP, GaP, GaAs, InAs, Si, Ge and sapphire after multiple pulse femtosecond laser irradiation in the wavelength range from 800 – 2100 nm. High spatial frequency periodic structures were observed on surfaces of InP, GaP, GaAs and sapphire. The periods of the structures were 4.2 – 5.1 times smaller than the free space wavelength of the incident radiation. Conditions required for formation of these ripple structures were identified.

The second series of experiments dealt with the analysis of the final state of the material after the cutting of grooves in InP under conditions potentially encountered in practical applications. The experiments can be grouped into three sets of investigations.

In the fourth set of investigations, the ablation rate for grooves micromachined with ≈ 150 fs pulses centered around 800 nm was investigated as a function of pulse energy, feed rate, number of passes over the same groove, and the light polarization relative to the cutting direction. A logarithmic dependence of the groove depth on the laser fluence was observed with two regimes characterized by different ablation rates and

different thresholds. The groove depth was found to be inversely proportional to the feed rate or equivalently, linearly proportional to the effective number of pulses delivered. With multiple passes over the same groove the depth was found to increase linearly up to approximately 20 consecutive passes. Above 20 passes the ablation rate decreased until a depth limit was asymptotically approached. The best results in terms of groove geometry and depth limit were obtained for grooves cut with the polarization of the beam perpendicular to the cutting direction.

In the fifth set of investigations, the residual strain fields resulting from laser micromachining of grooves in InP with femtosecond and nanosecond pulses centered around 800 nm were analyzed using a spatially resolved degree-of-polarization photoluminescence technique. Significant differences in the geometry of the strain patterns were observed in grooves machined in the two temporal domains. The experimental data were compared with results from a finite element model.

In the sixth set of investigations, grooves micromachined in InP with femtosecond and nanosecond pulses were investigated by cross-sectional transmission electron microscopy. Substantial densities of defects, extending over a few microns in depth, were observed beneath the grooves machined with femtosecond pulses. The high peak power density and the stress confinement caused by irradiation with femtosecond pulses, along with incubation effects, were identified as the major factors leading to the observed plastic deformations.

Preface

The work presented in this thesis has been previously published in the form of several refereed journal articles and one manuscript accepted for publication.

Paper 1:

Femtosecond laser pulse ablation of GaAs and InP: Studies utilizing scanning and transmission electron microscopy

A. Borowiec, M. MacKenzie, G.C. Weatherly, H. K. Haugen: Appl. Phys. A **77**, 411 (2003)

Paper 2:

Wavelength Dependence of the Single Pulse Femtosecond Ablation Threshold of Indium Phosphide in 400 – 2100 nm Range

A. Borowiec, H. F. Tiedje, H. K. Haugen: accepted for publication in Applied Surface Science, September 2004

Paper 3:

Subwavelength Ripple Formation on Surfaces of Compound Semiconductors Irradiated by Femtosecond Pulses

A. Borowiec, H. K. Haugen: Appl. Phys. Lett. **82**, 4462 (2003)

Paper 4:

Femtosecond Micromachining of Grooves in Indium Phosphide

A. Borowiec, H. K. Haugen: Appl. Phys. A **79**, 521 (2004)

Paper 5:

Imaging the Strain Fields Resulting from Laser Micromachining of Semiconductors

A. Borowiec, D. M. Bruce, D. T. Cassidy, H. K. Haugen: Appl. Phys. Lett. **83**, 225 (2003)

Paper 6:

Sub-surface Damage in Indium Phosphide Caused by Micromachining of Grooves with Femtosecond and Nanosecond Laser Pulses

A. Borowiec, M. Couillard, G. A. Botton, H. K. Haugen: Appl. Phys. A - Rapid Communication, **79**, 1887 (2004)

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Chapter 1

Introduction

1.1 Overview

Laser modification of semiconductors has been an area of intensive applied and fundamental research for over three decades. Research has been partially motivated by the possibility of laser applications in processing of semiconductors, especially in the electronics and optoelectronics industries. Examples of the processing techniques investigated include laser annealing, laser assisted chemical etching, laser deposition and laser removal of material also referred to as laser ablation. Experimental findings have stimulated interest in the understanding of the physical mechanisms behind laser-matter interaction, phase transformation and material removal after laser irradiation.

Many advances in the field of laser modification of semiconductors and other materials resulted from the development of amplified ultrashort pulse lasers within the past decade. In the context of laser science, the term ultrashort or ultrafast refers to the subset of pulsed lasers capable of producing light pulses with sub-picosecond pulse duration ($1 \text{ ps} = 10^{-12} \text{ s}$). Ultrafast laser pulses have a number of unique characteristics, which are particularly advantageous in high precision laser ablation. First, very high peak intensities can be achieved with relatively low pulse energies. For example, $1 \mu\text{J}$, 100 fs pulse focused to $10 \mu\text{m}$ spot diameter leads to peak intensity on the order of 10^{13} W/cm^2 . At such intensities, nonlinear optical processes become significant and lead to enhanced absorption, even in materials normally transparent at the laser wavelength. Second, the pulse width is shorter than the time required for hydrodynamic expansion and material removal. Consequently the energy deposition occurs at solid-state densities leading to very strong excitation. The effects of heat conduction can also be neglected on the timescale of laser-matter interaction. Furthermore, since the energy deposition and material removal are temporally separated there is no interaction of radiation with the ejected material. The combined effect is an enhancement in the localization of energy deposition leading to increased lateral and vertical precision of the ablated features with reduced heat and shock affected zones. During the past decade laser microprocessing or micromachining with ultrashort pulses has been shown to yield superior results compared to micromachining with nanosecond and longer pulse lasers. With constant advances in

ultrafast laser technology, femtosecond micromachining workstations are beginning to enter the mainstream industrial market.

The material presented in this thesis deals with femtosecond laser ablation and micromachining of indium phosphide (InP). InP is a widely used III-V compound semiconductor especially in optoelectronics and high-speed electronic applications. At the beginning of my graduate studies femtosecond laser modification and micromachining of InP had not been investigated and virtually no literature on the subject was available. The choice of InP was also influenced by the availability of high quality samples and the fact that the electronic, optical and physical properties of InP are very well characterized. Furthermore, InP is a direct bandgap semiconductor, which allows the use of optical analysis such as polarization resolved photoluminescence imaging. Lastly, many of the researchers in the Department of Engineering Physics at McMaster University use InP in device research, therefore any promising results and processing techniques developed would have been immediately transferable to device modification or repair.

1.2 Contributions to the Field

The work reported has been previously published in the form of five refereed journal articles and one manuscript accepted for publication, which address both the fundamental and the applied aspects of femtosecond laser ablation of InP. The experiments are most conveniently divided into two sets of investigations: the single and multiple pulse ablation of stationary samples described in Chapter 4, and micromachining and analysis of grooves cut in InP described in Chapter 5.

The first series of experiments dealt with scanning and transmission electron microscopy analysis of single-pulse laser ablation craters on the surfaces of InP and GaAs after irradiation with 130 fs light pulses at center wavelength around 800 nm. The ablation threshold fluences were also obtained for both compounds. The single-pulse ablation threshold measurements of InP were then extended to wavelengths of 400, 660, 1300 and 2100 nm. These studies were the first systematic investigation of the wavelength dependence of the ablation threshold in InP, covering the transparent and opaque regions of this semiconductor. In further studies of multiple pulse ablation of InP, high-spatial frequency periodic surface structures, commonly referred to as ripples, have been observed after irradiation of InP at wavelengths in the transparency region. The spatial periods of the ripples were substantially shorter than the wavelengths of the incident laser fields. Additional experiments were conducted on other compound and elemental semiconductors and conditions required for formation of these structures were identified.

The second set of experiments was a progression from single and multiple pulse irradiation of stationary samples to scribing and cutting of grooves in InP under conditions potentially encountered in practical applications. The ablation rate for micromachining of grooves in InP was investigated as a function of pulse energy, feed rate, number of passes over the same groove, and the light polarization relative to the cutting direction. This was the first systematic study of femtosecond laser

micromachining of InP. In further post mortem analysis, polarization and spatially resolved photoluminescence measurements were performed to image the strain fields resulting from femtosecond and nanosecond laser micromachining of grooves. Significant differences in the geometry of the strain patterns were observed in grooves machined in the two temporal domains. Further cross-sectional transmission electron microscopy analysis was conducted to study the details of the microstructure and the collateral damage in the vicinity of grooves micromachined by femtosecond and nanosecond laser pulses. These investigations were the first detailed studies of the residual strain and material microstructure in the vicinity of laser micromachined grooves.

I was the primary contributor to most of the experimental realization and writing of the majority of the manuscripts presented. I was responsible for the purchase, the design and the assembly of most of the experimental apparatus as well as building of the laser analysis tools, such as autocorrelators, frequency resolved optical gating setup and writing of all control and acquisition software. I performed all laser ablation and machining experiments as well as all scanning electron microscopy, optical microscopy and the data analysis. In all cases my supervisor Dr. Harold Haugen was instrumental in preparation of the final manuscript, and provided invaluable support and input on data analysis, interpretation of results, discussion and critical review. Several researchers in the departments of engineering physics and materials science at McMaster University collaborated with us and co-authored three publications presented in this thesis, they were Dr. George Weatherly and Dr. Maureen McKenzie, Dr. Daniel Cassidy and Dr. Doug Bruce, Dr. Martin Couillard and Dr. Gianluigi Botton. Acknowledgements specific to each publication will be included at the beginning of the section where each paper is presented.

1.3 Thesis Outline

Chapter 2 provides a brief literature review of the key experiments in the study of dynamics and the analysis of the final state of materials particularly relevant to experiments and results presented in this thesis. Chapter 3 includes the details of the laser system, experimental setup and the analytical techniques used in sample preparation and analysis. All experimental results published in the form of journal articles are included in Chapters 4 and 5. Due to the diversity of experiments performed, the discussion of potential follow up work is presented at the end of each section in Chapters 4 and 5. Chapter 6 concludes the thesis with a summary of the key results and provides a broader outlook for the field of femtosecond laser machining.

Chapter 2

Background

2.1 Introduction

This chapter includes a brief literature review of the key experiments in the study of the dynamics of ultrafast ablation and the analysis of the final state of InP after irradiation with femtosecond laser pulses. A more detailed literature review, specific to each set of experiments, can be found in each of the papers presented in Chapters 4 and 5. The current state of understanding of the ablation mechanism obtained from numerous experimental and theoretical investigations is also presented.

2.2 Literature Review

The behavior of semiconductors under intense optical excitation has been studied since the early development of lasers. The initial experiments were motivated by possibilities of using lasers in annealing of semiconductors, more specifically annealing of ion-implanted silicon [1]. Up to the late 1970s most of the investigations were performed with continuous wave and nanosecond lasers. Pulses in the picosecond range became available after the development of modelocked Nd:YAG lasers. Liu *et al.* performed the first experiments on the melting and resolidification of Si irradiated by 30 ps pulses at wavelengths of 532 and 266 nm [2]. In follow up experiments, Liu *et al.* investigated the phase transformation by time resolved reflectivity and charged particle emission techniques and reported evidence of carrier thermalization on a timescale shorter than 10^{-11} sec [3]. These results stimulated interest in ultrafast kinetics, especially phase transformation after intense optical excitation.

After the development of mode-locked dye lasers, pulse durations below 100 fs became available allowing time resolved measurements with femtosecond resolution. Most of the early work involved the study of the phase transformation by time resolved reflectivity and time resolved surface harmonic generation. The second harmonic generation in reflection from the medium can provide structural information related to the crystal symmetry [4]. Shank *et al.* applied this technique in the study of structural changes in silicon excited by 90 fs pulses and observed a transition from the crystalline to a disordered state in less than 1 ps [5]. In the following years several groups performed

similar experiments on silicon, gallium arsenide and carbon [6 – 9]. The experimental results provided evidence of ultrafast melting, which could not be explained by rapid thermal processes. The idea of nonthermal melting in the presence of a dense electron-hole plasma was proposed and investigated theoretically [10,11]. The model of the instability of a laser-excited diamond lattice developed by Stampfli and Bennemann predicted rapid melting when 15% of the valence electrons have been excited into the conduction band. Their calculations were consistent with experimental results in predicting the transition from a diamond lattice to a molten phase within 120 fs after laser excitation.

The next significant advance in laser technology was the development of Ti:sapphire lasers and the chirped pulse amplification (CPA) technique [12,13]. Currently Ti:sapphire is the crystal of choice in most amplified ultrafast lasers. Ti:sapphire has excellent optical and thermal properties, a high damage threshold and broad fluorescence bandwidth, which can support ~5 fs pulses. Pulse energies in the millijoule range are easily attainable via CPA. The CPA technique also allows the pulse duration to be varied from the femtosecond range to a few nanoseconds while keeping all other beam parameters constant. These aspects of the CPA technique provide a convenient method of studying the pulse width dependence of various physical processes. For example, Pronko *et al.* [14] studied the ablation dynamics with pulse width varying from 10 ns to 100 fs and observed a decrease in the ablation threshold with decreasing pulse duration. Similar experiments by other groups have also demonstrated the potential of femtosecond laser ablation as a tool for precision material modification [15,16]. Cutting, drilling and scribing with femtosecond lasers proved to yield superior results compared to machining with conventional lasers. However, the details of the physical mechanisms behind femtosecond laser ablation were still far from being understood.

The study of dynamics of semiconductors excited by femtosecond laser pulses was then extended to time-of-flight (TOF) mass spectroscopy in studies of melting and ablation of Si and GaAs [17,18]. The TOF experiments were supplemented with time resolved optical microscopy in studies of the transient state of matter during femtosecond laser ablation [19,20]. The experiments revealed that the removal of material after femtosecond irradiation occurs on a nanosecond time scale. The results were interpreted in terms of transient thermal processes.

Experiments based on the optical measurements have greatly increased the state of knowledge of the ablation process. However, structural information can only be deduced from optical measurements. The direct observation of the atomic structure requires the use of x-ray or electron diffraction. The availability of high peak power femtosecond lasers has led to the development of ultrafast x-ray sources and the techniques of temporally resolved x-ray diffraction were applied to the study of ablation dynamics [21 – 26]. The experimental results provided direct evidence of structural disordering on a femtosecond timescale. Most recently, the study of phase transformation dynamics was also extended to ultrafast electron diffraction [27], which allows observation of the short range order-disorder transition during phase transformation.

In addition to experimental work, numerous groups studied the ablation process analytically and numerically. Many models have been proposed to explain various

aspects of the femtosecond ablation process including: ultrafast laser pulse absorption by solid targets [28,29], femtosecond heating [30], expansion [31,32], stress generation [33,34], and defect capture and formation of periodic surface structures on semiconductor surfaces [35].

In recent years, a number of researchers applied molecular dynamics (MD) simulations to modeling of the ablation process [36 – 42]. In MD models, the material is described as a 2 or 3 dimensional lattice of interacting spheres, with translational and internal degrees of freedom. The motion and interaction is described by a classical formalism and in some cases a hybrid simulation approach involving MD and heat conduction [39]. MD simulations allow one to follow the evolution of the irradiated material from the energy deposition to the final state of the material. A number of predictions obtained from MD models have been confirmed experimentally including: decreases of the ablation threshold with decreasing pulse duration, the logarithmic dependence of the ablation rate on fluence and high transient pressures associated with the ablation process. Unfortunately, the limitation of MD models is the small cell sizes and full microscopic description of the ablation process is still beyond present computation capabilities. With ongoing advances in the computer technology MD models show a definite promise in aiding the understanding of the physics of ablation processes.

2.3 Dynamics of Femtosecond Laser Ablation

The experimental and theoretical investigations summarized above lead to a substantial improvement in the physical understanding of the ultrafast laser ablation process. The dynamics of the ablation process can be roughly divided into several stages: energy absorption, energy transfer to the lattice and subsequent material removal. A brief summary of each stage will be outlined below and a much more complete discussion can be found in Ref. 43, Chapter 13 and references therein.

2.3.1 Energy Absorption

The first step of the ablation process is deposition of energy into the material. In semiconductors the primary absorption mechanism involves excitation of electrons from the valance to the conduction band (interband) and free carrier absorption (intraband). The interband excitation can occur if the photon energy of the incident field is higher than the bandgap energy of the semiconductor. The bandgap of InP is 1.34 eV, which corresponds to wavelength of ≈ 930 nm. If the semiconductor is transparent at the laser wavelength the interband excitation can occur through nonlinear processes, such as multi-photon excitation and avalanche ionization, provided that the laser intensity is high enough. Nonlinear absorption is very important in femtosecond interaction due to the high intensity of the incoming radiation, on the order of $10^{12} - 10^{13}$ W/cm² near the ablation threshold [44,45].

Electrons promoted to the conduction band by linear or nonlinear excitation can absorb the laser energy via the process of free carrier absorption. If the kinetic energy

gained by the free electron exceeds the bandgap energy of the semiconductor, excitation of an additional electron across the bandgap can occur by impact ionization. The process is then repeated resulting in avalanche ionization and a rapid buildup of electrons in the conduction band. The free carrier absorption becomes significant with increasing density of electrons in the conduction band. Near the ablation threshold the carrier density in the conduction band of a semiconductor is on the order of 10^{22} cm^{-3} . The absorption depth for 800 nm radiation, estimated based on the Drude model, is on the order of 100 nm, which is comparable to the linear absorption depth in InP.

Of course, during the laser-material interaction all of the processes occur simultaneously and it is difficult to estimate the contribution of each channel. Due to the complexity of the process, it is also difficult to calculate or measure the effective penetration depth of the radiation and therefore the initial carrier distribution.

2.3.2 Energy Transfer

At the end of the laser pulse, electrons thermalize within the electron subsystem via carrier-carrier scattering in several tens of femtoseconds. The energy transfer from electrons to the lattice occurs via carrier-phonon scattering on a timescale ranging from a few 100 fs to a few picoseconds, depending on the material. Since the electrons and lattice are not in equilibrium this situation is often described by a two temperature model, where a distinction is made between the electron and the lattice temperature [16,43]. In the quantitative treatment, the energy transport by ballistic and diffusive propagation of electrons out of the laser interaction volume also has to be taken into account [45,46].

In semiconductors, energy transferred to the lattice leads to rapid melting. Time resolved experiments performed on Si [6], GaAs [7,17,18], InSb [23,47] and InP [48] indicate that melting can be thermal or nonthermal in nature depending on the excitation fluence. Both processes exhibit a definite threshold behavior. After the threshold fluence for thermal melting is exceeded the semiconductor will undergo a transition from the solid to liquid phase on a time scale of a few picoseconds. With a further increase in laser fluence non-thermal melting occurs in less than 1 ps. In InP irradiated with ~150 fs pulses, the thermal melting was observed in 1 – 2 ps while non-thermal melting was observed within 400 fs after irradiation. The nonthermal melting is attributed to excitation of a dense electron plasma in excess of 15% of the valence electrons, leading to destabilization of the diamond lattice [11]. Since the timescale for mass transport is significantly longer than for non-thermal or even thermal melting, the melted material is left at near solid state densities and a high initial temperature. The subsequent processes of material removal have been described in terms of transient thermal processes.

2.3.3 Subsequent Processes

Following melting, the hydrodynamic expansion of the ablated material begins a few 100 ps after the initial excitation [19,20]. In spite of numerous investigations the fundamental mechanisms leading to the material removal are still rather poorly understood. Several different ablation mechanisms were identified in theoretical investigations including: spallation, explosive boiling and vaporization [31,32,36 – 41].

The onset of a particular expansion mode depends on the amount of energy absorbed by the material.

Spallation occurs at a fluence slightly exceeding the ablation threshold, and refers to ejection of a complete layer of material induced by material fracture due to internal stress buildup brought on by constant volume heating. The pressure buildup is released by hydrodynamic expansion and emission of a strong pressure wave. The passage of the pressure wave leads to material fracture parallel to the surface of the sample.

At a higher fluence, or in materials where spallation might not apply, the expansion of material can occur through explosive boiling, also known as phase explosion. In phase explosion, the melted material enters a liquid-gas metastable state during expansion and homogenous nucleation of gas bubbles sets in, leading to formation of a heterogeneous phase of gas and liquid droplets. Phase explosion is believed to be the primary mechanism in femtosecond ablation below the threshold for plasma formation [42].

At a high enough excitation fluence the surface layer of the material can be completely atomized and material removal proceeds by process vaporization. In this case the term vaporization is used rather loosely as it does not refer to evaporation from the surface layer. Instead vaporization describes complete dissociation of the material as the energy absorbed exceeds the cohesive energy of the lattice.

2.3.4 Final State of Material

Despite the energy input in ~ 100 fs, the entire ablation process occurs on time scales of several 10 ns. For example, the resolidification time for InP is around ~ 25 ns [48]. The final state of the material, i.e. morphology, crystal structure and chemical composition, depends on the amount of absorbed energy, material removal mechanism and subsequent cooling rates. Ablation experiments are usually performed with laser beams that have a near Gaussian spatial profile, therefore energy deposition varies across sample surface. Due to the threshold nature of ultrafast ablation processes, several characteristic morphological regions are typically observed within an area irradiated by a single pulse. In post mortem analysis, characterization of the fluence dependence of the lateral dimensions of various features, crater profiles, local changes in crystallography and chemistry can be related to various dynamical mechanisms. For example, changes in crystal structure, such as, formation of amorphous or polycrystalline regions, can be related to the local heating and cooling rates. Formation of crystal defects can be related to peak pressures attained during the ablation process, and the analysis of the depth of the ablation craters can provide an estimate of the energy deposition profiles.

In addition to purely fundamental studies, the post mortem analysis can provide a wealth of information relevant for practical applications of lasers in material processing and micromachining. For example, the ablation threshold and ablation rates can be readily obtained from the analysis of the final state by measuring the fluence dependence of the ablated volume or crater depths. Changes in mechanical, optical and chemical properties of the samples can have important consequences in various applications and can put limits on the applicability of the laser machining. Alternatively, laser

modification of chemical and physical properties of surfaces might be beneficial in some applications.

2.4 Laser Ablation and Processing of InP

In recent years, nanosecond and picosecond laser processing of InP has been reported by a few groups. The investigations include laser-induced order-disorder transitions [49], laser-stimulated nonthermal particle emission from InP surfaces [50], electronic desorption from InP surfaces [51] and soft laser sputtering of InP surface irradiated with nanosecond laser pulses [52]. Bonse *et al.* [53] reported the first work on femtosecond laser ablation of InP. The authors measured the ablation rates and the ablation thresholds of InP after irradiation with 130 fs, 800 nm pulses. Argument *et al.* [54] performed a similar set of measurements and their results were in good agreement with work reported by authors in Ref. 53. In subsequent experiments the detailed studies of the final state of InP after femtosecond irradiation were performed with optical, scanning probe microscopy and micro-Raman spectroscopy [55,56]. In parallel studies utilizing transmission electron microscopy of single pulse ablation craters were reported [57] with the emphasis on characterization of the microstructure and the chemical composition of the ablation craters. Experiments on multiple pulse irradiation of InP with femtosecond laser pulses centered around 1300 nm and 2100 nm revealed the formation of high spatial frequency ripple structures on the surface of InP and other compound semiconductors [58]. Similar structures were previously observed on surfaces of various dielectrics and ceramics [59– 64]. The spatial period of these ripples was significantly smaller than the wavelength of the incident light in contrast to classic ripple structures where the spatial period is close to the wavelength of the excitation pulse [65 – 67].

The experiments involving irradiation of stationary targets were followed by a study involving micromachining of grooves where the sample was translated at constant speed relative to the stationary laser beam [68]. The main goal of these experiments was analysis of the ablation rate and morphology of grooves. The analysis was also extended to analysis of strain fields resulting from laser micromachining of grooves in InP. The method of polarization resolved photoluminescence was applied in the analysis and revealed significant differences between grooves machined with femtosecond and nanosecond pulses [69].

In addition to laser ablation, work on laser-assisted dry etching of InP involving the use of excimer lasers in the presence of a halogen atmosphere has been reported [70, 71]. Prasad *et al.* [70] used a gas mixture of chlorine diluted in helium in an investigation of etch rates with 308 nm irradiation. Laser-assisted (308 nm) dry etching of InP in low-pressure chlorine atmospheres at fluences lower than the ablation threshold have been studied by Wrobel *et al.* [71]. Matz *et al.* have demonstrated a practical application of this technique in dry etching of integrated InP micro-lenses using a 248 nm excimer laser [72]. These chemically-assisted laser etch schemes using nanosecond UV lasers offer an interesting, complementary approach to direct writing with femtosecond laser pulses. Bäuerle [43] provides a comprehensive overview of theory and experiments of laser assisted etching.

Currently, semiconductor processing largely involves well-established photolithography technology and it is unlikely that direct laser patterning would replace it in the near future. However, the ultrafast laser ablation can play an important role in dicing [73], prototyping, device repair [74] and semiconductor failure analysis, where successive layers can be precisely removed to expose transistor layers in a die.

Chapter 3

Experimental Setup and Procedure

3.1 Introduction

This chapter provides the description of the femtosecond laser system, the ablation setup and the experimental method, and all diagnostic tools used in sample analysis.

3.2 Femtosecond Laser System

All experiments reported in this thesis were performed with a commercial amplified Ti:sapphire laser system, that consists of a femtosecond oscillator, a regenerative amplifier and an optical parametric amplifier pumped by a separate femtosecond amplifier.

3.2.1 Femtosecond Oscillator

The first part of the laser system is the Tsunami Ti:sapphire oscillator (Spectra Physics). Tsunami is pumped longitudinally by the Millennia V (Spectra Physics) - neodymium yttrium vanadate (Nd:YVO_4) laser at a wavelength around 532 nm. The Tsunami produces 10 nJ, 90 fs pulses at a repetition rate of 82 MHz centered around the wavelength of 800 nm with a ~ 10 nm bandwidth (full width at half maximum). Under typical operating conditions only ~ 3 nJ are required to seed the amplifier.

3.2.2 Femtosecond Amplifier

The second part of the laser system is the Spitfire LCX Ti:sapphire regenerative chirped pulse amplifier (Spectra Physics). The majority of the amplifier systems in use today are based on a chirped pulse amplification (CPA) process [12,13]. Ultrafast pulses cannot be amplified directly since the peak intensity would exceed the damage threshold of optical components during the amplification process. This problem is avoided in CPA by stretching the pulse in time prior to amplification, hence lowering the peak intensity below the damage threshold of the optical components. The pulses are stretched in time by introducing a specific amount of dispersion with a grating or prism stretcher. The stretched pulse is then amplified in a multi-pass amplifier cavity. After amplification the

pulse is recompressed approximately to the original duration by a grating or prism compressor. The principle of CPA process is shown in Fig. 3.1 with pulse durations and pulse energies typical of the Spitfire LCX amplifier.

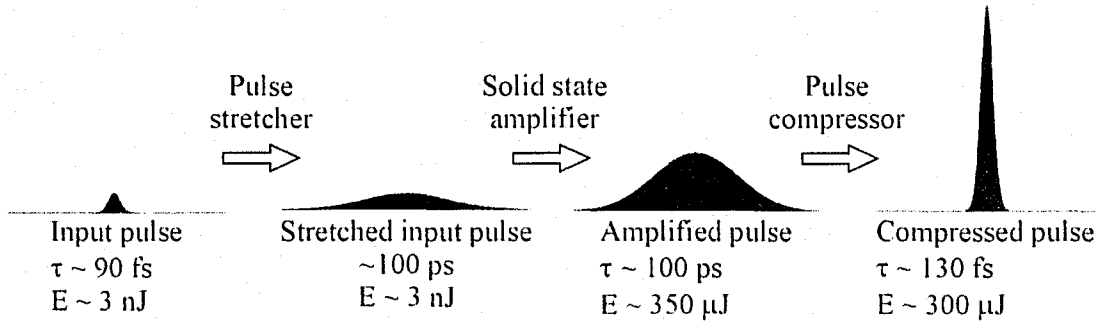


Figure 3.1: The principle of the chirped pulse amplification (CPA) process. Pulse durations and pulse energies shown at each stage are typical for the Spitfire LCX.

A schematic of the Spitfire LCX cavity is shown in Fig. 3.2. The input pulses are stretched from ~ 90 fs to ~ 100 ps, resulting in reduction of the peak pulse intensity by a factor of $\sim 10^3$. The stretched, s-polarized train of pulses is coupled into the amplifier cavity by a reflection off the Ti:sapphire crystal facet. The first Pockels cell (PC1) is activated for ~ 10 ns and the polarization of a single pulse is rotated from s- to p-polarization. The amplifier cavity is designed for p-polarized operation; therefore only the rotated pulse will match this condition and the rest will experience high loss. The Ti:sapphire crystal is pumped by a pulsed 5 mJ Nd:YLF laser, a Merlin (Positive Light) operating at a 1 kHz repetition rate. In a single pass through the crystal the pulse energy only increases by a factor of 2 – 3. Therefore amplification by a factor of $\sim 10^5$ requires multiple passes through the crystal. The buildup of the energy inside the cavity is monitored by a photodiode (PD) located behind one of the cavity mirrors. The pulse circulates in the cavity until gain saturation is reached. Once the saturation is reached, the second Pockels cell (PC2) is activated and the polarization of the amplified pulse is rotated from p- to s-polarization. The amplified pulse is ejected from the cavity by reflection from the thin film polarizer (TFP) and recompressed to ~ 130 fs with a grating compressor.

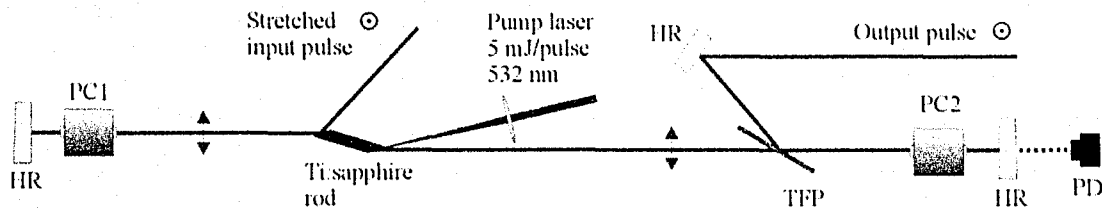


Figure 3.2: Schematic of Spitfire LCX amplifier cavity. HR – high reflector, TFP – thin film polarizer, PC – Pockels cell, PD – monitor photodiode.

Chirped pulse amplification enables access to pulse durations spanning several orders of magnitude while maintaining all other laser parameters constant, such as

wavelength, pulse energy and spatial beam profile. Fully compressed pulses have pulse widths around 130 fs and the pulse duration can be increased up to ~100 ps by detuning the grating compressor. In the absence of a short seed pulse, the lasing action is initiated by spontaneous emission and a pulse duration ≈ 8 ns can be obtained in this mode of operation. Nanosecond pulses obtained from an unseeded amplifier were used in several experiments aimed at comparison of laser machining in femtosecond and nanosecond temporal domains. The same method was previously used in studies of pulse width dependence of laser ablation and micromachining [14,16].

Typically the amplifier was operated at the center wavelength of 800 nm. In a number of experiments, 400 nm pulses were obtained by frequency doubling the output of the Spitfire beam in a 0.3 mm beta barium borate (BBO) crystal cut for type I phase matching.

3.2.3 The Optical Parametric Amplifier (OPA)

The high intensity of femtosecond pulses allows for very efficient conversion to near infrared wavelengths in the range of 1100 – 3000 nm using an optical parametric amplification process (OPA). The OPA is based on difference-frequency mixing of two beams in a nonlinear crystal. A weak signal beam at frequency ω_s is sent through the crystal in the presence of an intense pump beam at frequency ω_p , where $\omega_p > \omega_s$. During propagation through the crystal, energy is transferred from the pump beam to the signal beam. In addition a third beam is generated radiating at the difference frequency $\omega_i = (\omega_p - \omega_s)$, commonly called the idler beam. The signal and idler beams have perpendicular polarizations and can be easily separated by polarization sensitive optics. A typical near infrared OPA, pumped by a Ti:sapphire laser around 800 nm, provides a signal wavelength between 1100 - 1600 nm and an idler wavelength between 1600 - 3000 nm.

In all experiments presented in this thesis, pulses in the 1100 – 3000 nm wavelength range were obtained from a commercial OPA – 800 (Spectra Physics), which was pumped by a sub-50 fs Spitfire (Spectra Physics). The signal and idler beams were typically tuned to wavelengths around 1300 nm and 2100 nm respectively. Further wavelength extension is possible by frequency doubling the signal and idler beams. In some experiments, pulses centered around 660 nm were obtained by frequency doubling the signal beam in a 2 mm BBO crystal cut for type I phase matching.

3.3 Laser Ablation Setup

The schematic of the beam delivery and the ablation setup is shown in Fig. 3.3.

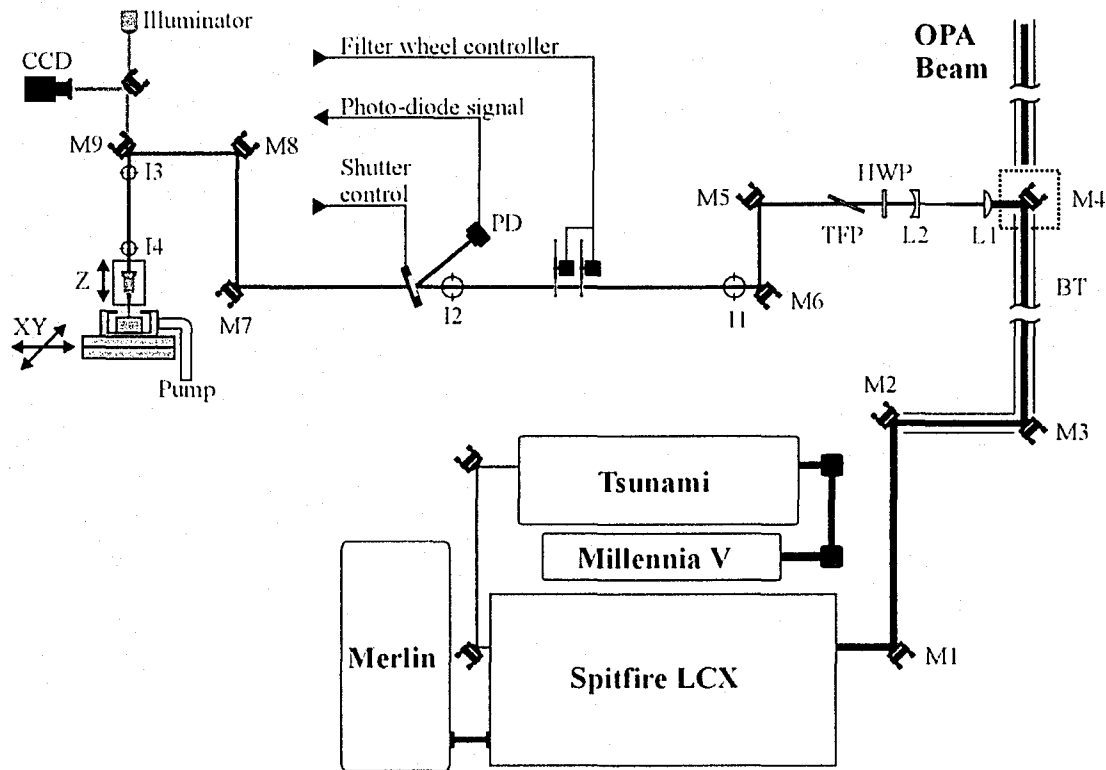


Figure 3.3: Schematic of the beam delivery and the ablation setup, M – mirror, BT – beam tube, L – lens, I – iris, PD – photodiode, HWP – half wave plate, TFP – thin film polarizer.

The beam from the Spitfire was directed to the ablation setup by four dielectric mirrors (M1-M4) and the OPA beam was brought from the opposite end of the table by two gold mirrors. Mirror M4 was mounted on a kinematic base plate and allowed us to easily select either the OPA or Spitfire beam. Since the beams traveled several meters between the lasers and the ablation setup they were enclosed in beam tubes (BT) to minimize instability caused by air currents. The selected beam, which was initially ≈ 10 mm in diameter, was reduced in size by a beam condenser, constructed from a $f = 50$ cm achromatic doublet (L1), and a $f = -20$ cm plano-concave singlet lens (L2), to a diameter of ≈ 4 mm. The typical beam profile of an 800 nm beam after the second lens L2 is shown in Fig 3.5. The pulse energy of the Spitfire was typically between 200 – 300 μJ , which is at least two orders of magnitude higher than required for most experiments. Therefore, the initial pulse energy of 800 nm beam was adjusted to 1 – 10 μJ with a zero order half wave plate (HWP - 0RP44-3, Newport) and a thin film polarizer (TFP - 11B00UP.26, Newport). In experiments performed with pulses at 400 nm, the 0.3 mm beta barium borate (BBO) crystal was placed after the thin film polarizer. The initial energy of pulses at 400 nm was controlled by adjusting the pulse energy of the Spitfire beam. In experiments utilizing pulses from the OPA, the half wave plate and polarizer were removed since the maximum pulse energy was typically less than 20 μJ for both

signal and idler beams. After the polarizer, the dielectric mirrors M5 and M6, chosen for an appropriate wavelength, were used to align the beam through irises I1 and I2 before the main setup. During the experiments, the pulse energy was controlled with a set of 1 mm thick, reflective, neutral density filters (Model 5249, New Focus). The filters were mounted in two filter wheels and allowed power adjustments in optical density steps (OD) of 0.1 ($OD = \log(I/I_0)$ where I is the laser intensity). The two filter wheels were mounted on custom built rotation stages and the position of each of the wheels was controlled manually or by computer via an RS-232 interface. While using a half-wave plate and a polarizer would have allowed the power to be varied continuously, the neutral density filters were chosen since we routinely worked with a wide range of wavelengths. The neutral density filters have a relatively flat response between 400 – 3000 nm and were much more cost effective and practical than multiple sets of waveplates and polarizers.

The laser exposure time (or the number of pulses delivered to the sample) was controlled by a mechanical shutter (VS25 with VMM-D1 controller, Uniblitz). The shutter had a minimum exposure time of 10 ms. Shutter blades are made of highly polished stainless steel and while the shutter was closed the beam was reflected onto a photodiode (PD). The photodiode was used to monitor the intensity of the laser during experiments. The calibration procedure of the photodiode is discussed in Section 3.4.1. Beyond the shutter, the beam was delivered to the focusing optic by two silver mirrors, M7, M8 and one dielectric mirror M9. In several early experiments a 10× microscope objective (M - 10×, Newport) was used as a focusing optic. However, in most of the experiments the focusing optic was a 5× microscope objective (M - 5×, Newport). The use of this objective allowed focusing of the laser to a spot diameter of approximately 10 μm , with a working distance of roughly 1.5 cm. The long working distance was required for focusing the beam inside of the vacuum chamber through the chamber window. The vacuum chamber was a custom machined, aluminum vessel with 1 mm uncoated, fused silica window. In most of the work reported in this thesis, the sample chamber was mounted on XY translation stages (UTM150PE.1, Newport) and the focusing objective was mounted on a separate Z translation stage (M-MFN25PP, Newport). The stages were controlled by ESP300 controller (Newport) via GPIB interface. The timing, synchronization and data acquisition were performed by a computer through general purpose data acquisition card (PCI-6025E, National Instrument). The control software was custom written in Visual C++ to allow full automation of most of the experiments. A dielectric mirror M9 was a high reflector at a laser wavelength but transparent in the visible region. A confocal CCD camera arrangement, aligned through the dielectric mirror M9, was used to monitor the sample alignment and the machining process during the course of the experiments.

3.3.1 X-ray Emission from Femtosecond Laser Machining

Focusing high energy femtosecond pulses to a spot size near the diffraction limit on a solid target leads to the generation of very hot plasmas at near solid state density. The emission from plasmas generated by ultrafast laser pulses can span an energy scale

from vacuum ultraviolet (VUV), soft x-ray [75], to hard x-ray [76] up to MeV photons [77] depending on the excitation fluence. In previous studies, we have investigated x-ray emission resulting from irradiation of solid targets under typical micromachining conditions [78]. We have shown that $\sim 300 \mu\text{J}$ pulses can excite x-rays with the high energy tail extending up to 25 keV. The majority of the radiation was emitted below 10 keV with the radiation distribution approximated by a blackbody source at 8.9 MK. Recently, Hagedorn *et al.* presented similar results in analysis of x-ray generation with sub-millijoule femtosecond laser operating at 1 kHz repetition rate [79]. Also, Thoss *et al.* [80] and Jiang *et al.* [81] have recently reported on hard x-ray generation with kilohertz repetition rate systems. Although most of our micromachining experiments were carried out with pulse energies below 10 μJ , precautions were taken to ensure a safe operating environment even under maximum pulse energy irradiation. The micromachining setup was shielded by a 3 mm thick stainless steel sheet from the back side and leaded acrylic, equivalent to a 0.3 mm of lead, from the front. Furthermore, in most experiments, even those conducted at ambient pressure, the samples were placed inside sample chamber providing almost complete shielding.

3.3.2 Vibration and Mechanical Stability

The micromachining setup and the two laser systems were located on separate optical tables. Due to relatively large distance between the lasers and the micromachining setup, care was taken to minimize all sources of mechanical or environmental instabilities. The majority of the beam path between the lasers and the micromachining setup was enclosed in beam tubes to avoid pointing instabilities caused by air currents. Optical enclosures were built around the machining setup to further reduce this problem and protect optics from dust. The enclosures also block any stray beams reflected or scattered off polarizers, neutral density filters and other optics. Thus in addition to laser safety glasses, the optical enclosures provide an additional level of eye protection.

The low frequency vibrations caused by external sources, such as traffic, construction and building vibrations, were quantified by analyzing test patterns micromachined with a high power objective. A typical test pattern included grids of lines with spacing of 3 – 5 μm machined with a 50 $\times$ objective (M Plan NIR 50 $\times$, Mitutoyo). Mechanical vibrations lead to irregularities in the grid spacing. Based on such tests, the upper limit on the amplitude of mechanical vibrations was determined to be $\pm 1 \mu\text{m}$.

3.4 Laser Diagnostic Tools

3.4.1 Power Measurements

Accurate power measurements were very important since the goal of many investigations was determination of the ablation thresholds and characterizing the dependence of various machining parameters on pulse energy or more generally energy density or fluence. The power measurements in the wavelength range from 400 – 1000 nm and 1300 – 2000 nm were performed with a semiconductor power meter PD300-3W (Ophir) and with a surface absorbing detector head 2A-SH (Ophir) respectively. The

accuracies of the semiconductor and the surface absorbing power meter heads were quoted as $\pm 5\%$ and $\pm 3\%$ respectively in the wavelength ranges of interest. Fig. 3.4 shows an example of power measurements at 800 nm made at 20 different neutral density filter settings with two different semiconductor heads and the thermal head. Measurements made with three different heads agreed to within $\pm 3\%$ over the entire range of pulse energies. These measurements also confirm the accuracy of the neutral density filters provided by the manufacturer.

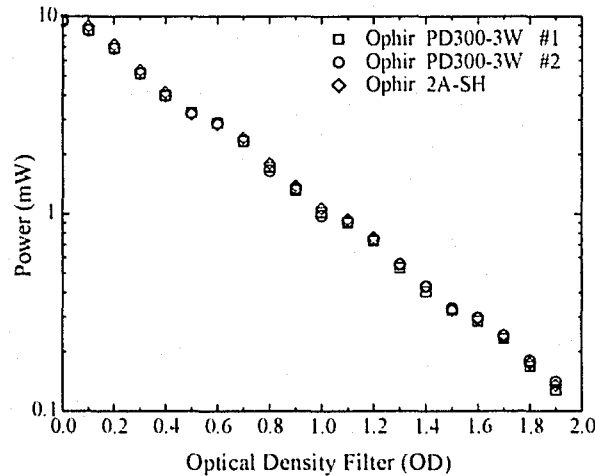


Figure 3.4: Power measurements made at 800 nm, with three different power meters and OD filter settings ranging from OD = 0.0 to OD = 2.0.

All meters used measure the average power and have a response time from 0.3 to 1 second and, hence, cannot directly measure the energy of individual pulses. The pulse energy can be calculated by dividing the average power measured by the repetition rate of the laser (1 kHz).

In all experiments, the power (pulse energy) was always measured after the microscope objective and the sample chamber window to account for all throughput losses. Before each experiment, the power measurements were made at all filter wheel settings from OD = 0.0 to OD = 2.0 as shown in Fig. 3.4. To account for power fluctuations or drifts, the power was also measured with the calibrated photodiode (see Fig. 3.3) during the course of experiments. The photodiode calibration sequence was performed as follows:

- First the power after the microscope objective and the window was measured by a computer based strip chart program for a period of 5 minutes and the average power (P_{avr}) and the standard deviation (σ_P) were calculated.
- After the power measurement, the shutter was closed, reflecting the beam onto the photodiode and the photodiode signal was measured for a period of 5 minutes. The average signal level (S_{avr}) and the standard deviation were determined (σ_S).
- During the course of the experiments, the photodiode signal level (S) was monitored and the power was calculated by $P = S \cdot (P_{avr}/S_{avr})$.

The obvious disadvantage of this calibration procedure is the fact that the photodiode reading was not taken at the exactly same time as the power meter reading. This would

have been problematic in a case of severe laser intensity fluctuations or significant drift of the output power over a period of several minutes. In practice, this was never a problem. The calibration sequence was also performed several times during the course of the day to check for any inconsistencies. In all cases, the photodiode measurements were compared with the measurements performed with the power meter. The NOVA display unit (Ophir) has an RS-232 interface and the entire calibration process was automated with custom software written in Visual C++.

3.4.2 Alignment of the Focusing Objective

Prior to every experiment it was necessary to ensure that the laser was properly focused on the sample surface. The position of the focus was determined by micromachining sets of lines on a Si test sample while monitoring the machining process by a CCD imaging system. During the machining of lines, the pulse energy was decreased until no surface modification was observed and then increased to slightly exceed the threshold for visible modification. At this point, adjustment of the focusing objective relative to the sample surface led to changes in the laser spot size and hence changes in the fluence. If the objective was at optimum focus, moving the objective up or down led to defocusing, hence an increase in the spot size on the surface and a decrease in the fluence below the modification threshold. Conversely, if the objective was not at the optimum position, moving it either up or down led to an improved focus and an enhancement in machining. The process was repeated several times until an optimum position of the objective relative to the sample surface was identified. The focus of the CCD camera was then adjusted to coincide with the optimum laser focus. After a new sample was inserted into the chamber the microscope position was adjusted until the sample appeared in good focus on the TV monitor. This method is still subjective as the sample appears in focus over the distance of several microns, corresponding to the depth of focus of the objective. Due to this inherent uncertainty single pulse ablation measurements were performed on every sample to measure the laser spot size on the sample surface prior to every experiment. The method of spot size measurement is described in section 3.4.4.

3.4.3 Beam Profile Measurements

The spatial profile of the beam was characterized with a Si CCD beam profiler (BeamStar, OPHIR). The same camera was also used to measure the intensity distribution of the infrared signal and the idler pulses (1300 and 2100 nm) in a manner described by Briggman *et al.* [88]. Under most of the experimental conditions the beam profile and the far field profile after the microscope objective closely followed a Gaussian intensity distribution. Fig. 3.5 shows a typical beam profile of the Spitfire beam after the beam condenser (see Fig. 3.3).

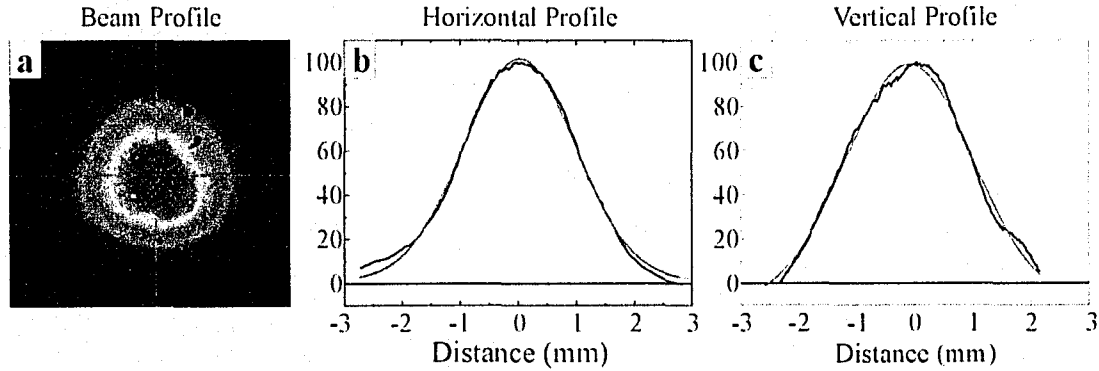


Figure 3.5: (a) Typical beam profile of the Spitfire beam (800 nm wavelength) after beam condenser (see Fig. 3.3) taken with the OPHIR BeamStar CCD beam profiler. The red curve in figures (b) and (c) represents a Gaussian fit to the intensity distribution along the horizontal and the vertical direction.

3.4.4 Spot Size Measurements

Determination of the laser fluence is essential for characterization of the ablation process. The peak fluence of a Gaussian beam is given by

$$\phi_o = \frac{2 \cdot E_o}{\pi \omega_o^2}, \quad (3.1)$$

where E_o is the pulse energy and ω_o is the spot size, i.e., beam radius measured at $1/e^2$ of the intensity profile. The accuracy of fluence determination largely depends on the measurements of the spot size on the sample surface. For tightly focused beams, direct measurement with a CCD beam profiler (see Section 3.4.3) is limited to relatively large beams since the typical CCD pixel size is in the range of 20 μm . Specialized CCD beam profilers for measuring tightly focused beams are available commercially (e.g. Duma Optonics Inc). These instruments are rather expensive and impractical for *in situ* measurements and were not available in our laboratory.

The spot size of tightly focused beams can also be determined by scanning a knife-edge through the focused beam and measuring the total transmitted signal as a function of the lateral coordinate of the knife-edge [82– 84]. Although this technique yields good results, in practice it is difficult to make these measurements *in situ* for tightly focused beams, especially ensuring that the plane of the knife-edge scan coincides with the sample surface.

Lui [85] introduced a convenient technique for measuring spot size of tightly focused beams by analysis of the lateral dimensions of the ablation craters. This method was adapted by many groups studying laser ablation and micromachining as it also allows one to determine the modification threshold of the target material. The diameter (D) of the ablation crater is related to the energy of the incident pulse by [53]

$$D^2 = 2 \omega_o^2 \ln \left(\frac{E_o}{E_{th}} \right), \quad (3.2)$$

where E_{th} is the threshold pulse energy, that is a minimum pulse energy required to produce permanent material modification. In the analysis, a set of single pulse ablation craters produced with decreasing pulse energy were prepared on the sample. The crater diameters were measured as a function of the pulse energy E_o ; then E_{th} and ω_o were determined by fitting the data to Eq. (3.2). With the obtained fit parameters the threshold fluence was calculated with Eq. (3.1). A typical set of experimental data is shown in Fig. 3.6, obtained for InP irradiated by 130 fs, 800 nm pulses, focused with a 5 $\times$ objective. The solid line represents the fit to Eq. (3.2).

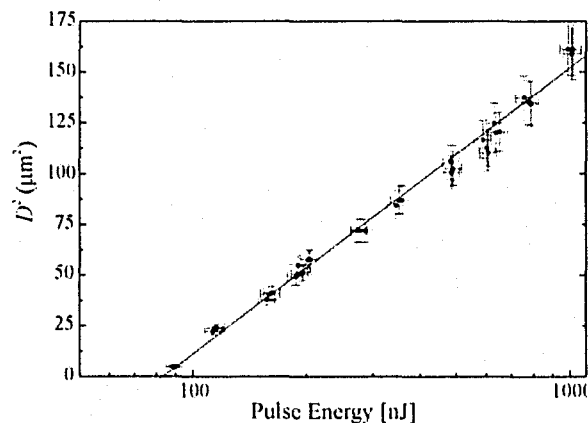


Figure 3.6: Spot size measurements of beam focused on the sample surface by a 5 $\times$ objective.

In this particular experiment, the least squares fit yields a spot size of $5.46 \pm 0.05 \mu\text{m}$. In a larger set of experiments performed over the course of four years, the spot size after the 5 $\times$ objective varied from 5 to 6 μm . This variation is attributed to the inherent uncertainty in sample positioning with respect to the objective (Section 3.4.2) and changes in the beam size before the objective.

In addition to my experiments, two other graduate students have undertaken femtosecond laser ablation research in recent years using the same experimental setup. During the course of their experiments, they have also consistently measured spot sizes of approximately 5.5 μm in the ablation of Si and various metals. Comparison of independent measurements performed with this technique over period of months by different people can put an upper limit on the uncertainty in spot size measurement of $\pm 0.5 \mu\text{m}$, although the uncertainty in any given measurement is expected to be significantly better.

The threshold energy obtained from the fit depends on the choice of the morphological feature of the crater followed in the extrapolation. Single pulse irradiation with pulse energies exceeding the modification threshold leads to the formation of several characteristic morphological regions. These regions can be associated with various physical processes, for example melting and ablation, and were investigated extensively in InP [55]. Irrespective of the feature chosen in the extrapolation, the spot size obtained from the fit should always be the same. Fig. 3.7 shows an example of measurement performed on InP irradiated with 130 fs, 800 nm pulses and the $f = 50 \text{ cm}$ plano-convex

lens used as a focusing objective. The crater measurements were performed with an optical microscope (Section 3.5.3).

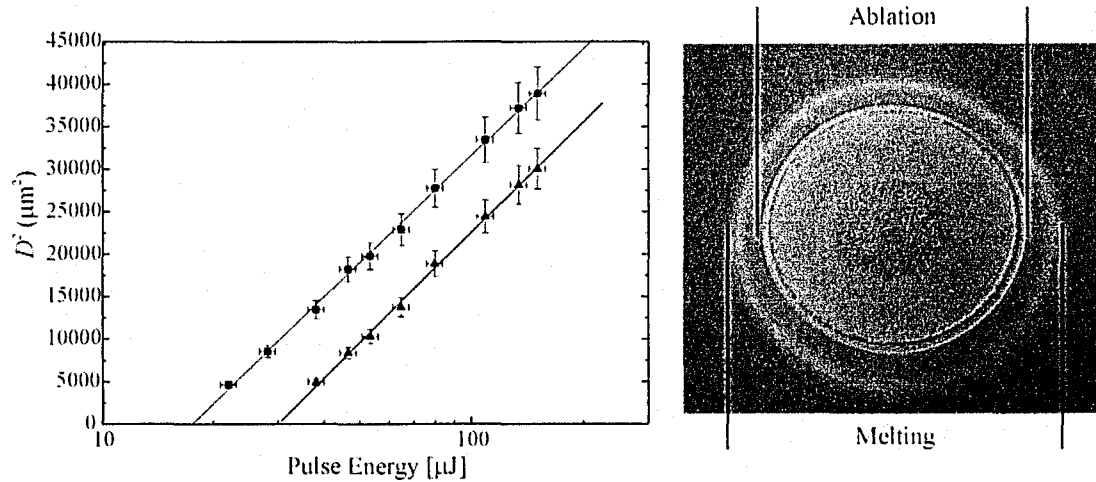


Figure 3.7: Outer diameters (D^2) of two different modification zones of the irradiated surface of InP, corresponding to melting and ablation regions indicated in the optical microscope image on the right side. The solid lines represent least squares fit to Eq. 3.2.

The outside diameters of two different morphological features, indicated in the optical micrograph in Fig. 3.7, were followed in the extrapolation. The outer feature corresponds to a melted region and the inner feature, surrounded by a rim, marks the boundary of the ablated area [55]. In both cases the spot size was measured to be $\omega_s = 96 \mu\text{m}$. An independent knife-edge measurement performed in the same setup yield a spot size of $\omega_s = 105 \mu\text{m}$ which is in good agreement with values obtained from D^2 fit.

Craters produced with tightly focused beams were almost exclusively measured with a scanning electron microscope (SEM). The melted zone was very difficult to observe with the SEM and the crater rim was the most distinct feature. Under tight focusing conditions the rim thickness is significant compared to the total dimensions of the crater, hence measuring the inside and outside crater diameter yields somewhat different thresholds as shown in Fig. 3.8. In this set of measurements, the spot size obtained from the two fits yields $5.1 \pm 0.1 \mu\text{m}$ and $4.9 \pm 0.1 \mu\text{m}$ for outside and inside diameters respectively. In all experimental measurements presented in this thesis the crater diameters were always measured to the outside rim diameter. This feature provided highest contrast and was most easily identified under all microscopy techniques.

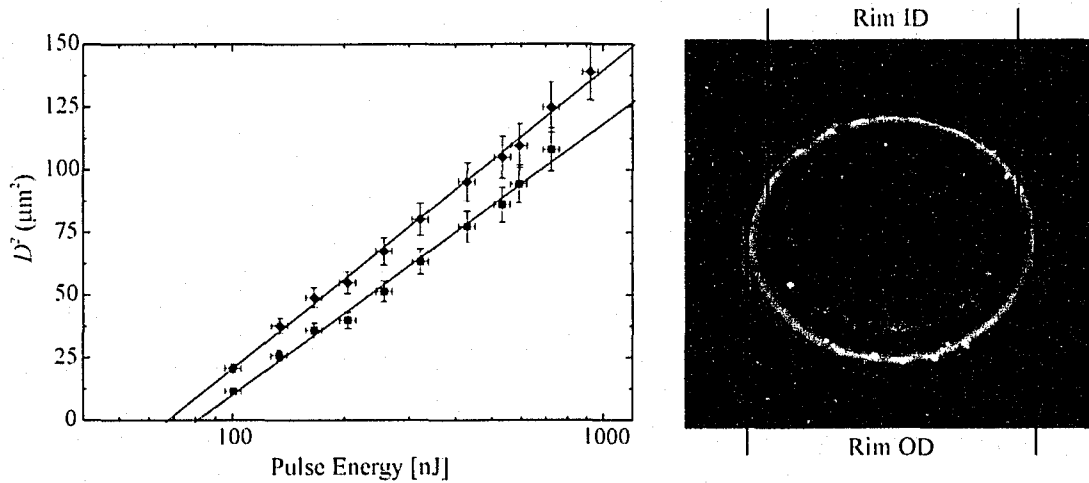


Figure 3.8: Outer diameters (D^2) of two different morphological features of the crater shown in the SEM image produced by irradiation of InP with tightly focused beam. The solid lines represent least squares fits to Eq. 3.2.

A test of a possible dependence of the measured threshold on the laser spot size was conducted on InP by varying the position of the 5× objective relative to the sample surface. Figure 3.9 shows single pulse ablation measurements in the range of spot sizes of 5.5 to 20.8 μm . A maximum variation of the threshold fluence of only $\approx 10\%$ was observed, with no indication of a definite trend.

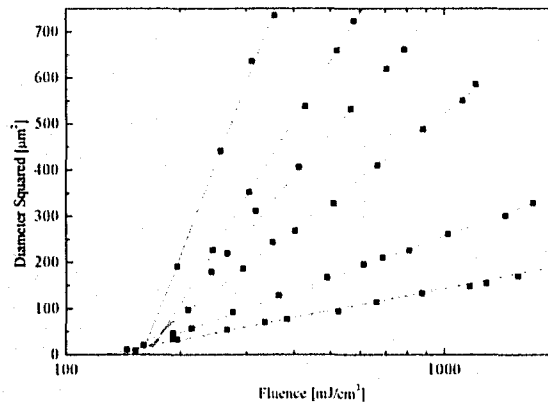


Figure 3.9: Six sets of D^2 measurements with a laser beam focused on the sample surface by a 5× objective at various separations relative to the sample surface.

3.4.5 Spectrum Measurements

Spectral measurements in the visible wavelength range were performed with an array spectrometer PC2000 (Ocean Optics). Spectral measurements in the near infrared (1000 – 2200 nm) were performed with a scanning grating spectrometer Model 9050 (Science Tech), equipped with a 600 line/mm grating and an InAs detector with a silicon

filter. The spectral resolution of both of these instruments was better than 1 nm. Typical spectra of beams around 400, 660, 800, 1300 and 2100 nm are shown in Fig. 3.10.

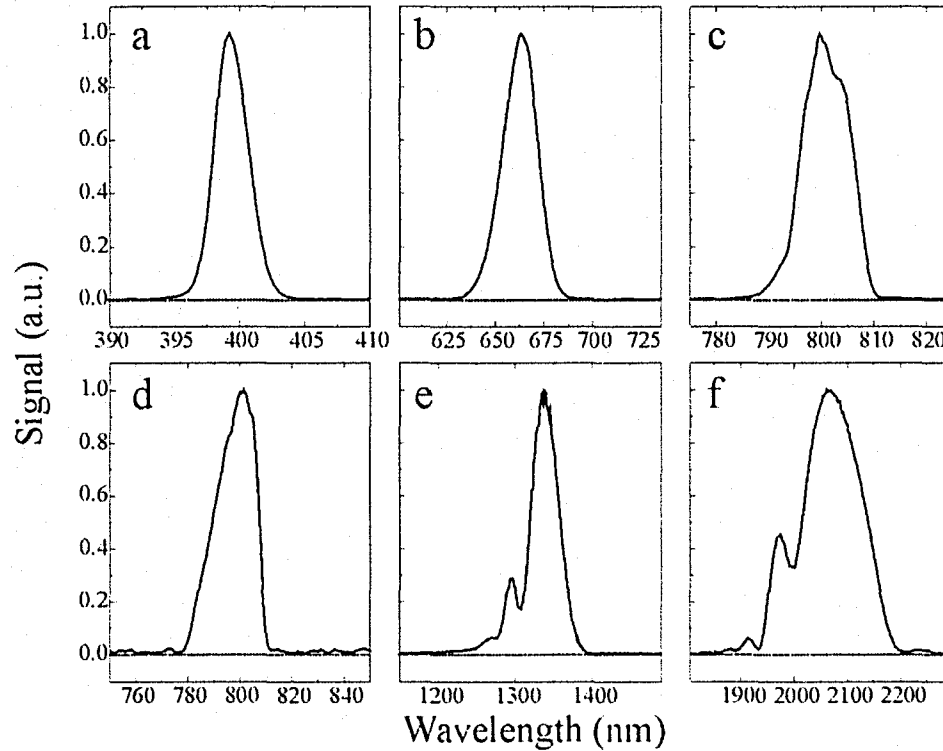


Figure 3.10: Typical spectra of: (a) second harmonic of the Spitfire after frequency doubling in 0.3 mm BBO crystal, (b) second harmonic of the OPA signal beam frequency doubled in 2 mm BBO crystal, (c) 130 fs output of the Spitfire, (d) unseeded Spitfire operating in nanosecond mode, (e) OPA signal beam, (f) OPA idler beam.

3.4.6 Pulse Width Measurements

The measurement and characterization of ultrashort laser pulses is a non-trivial problem and it has been an active field of research in itself. The majority of measurement techniques rely on various autocorrelation schemes. A very good overview of these techniques can be found in a number of textbooks [86,87]. In experiments presented in this thesis, interferometric and intensity autocorrelation were routinely used for pulse width measurements. The autocorrelator was a home built instrument based on a Michelson interferometer configuration. The input beam was split into two replicas by a broadband, 1 mm thick beam splitter (FO002, Femtolasers). The beam in each arm was retro-reflected by a gold mirror and the two beams were recombined by the same beam splitter. In the interferometric configuration the two beams were superimposed and sent through a nonlinear crystal. In the intensity or background free configuration the beam in one arm was horizontally displaced by ~ 4 mm relative to the other beam. The two parallel beams were recombined by the same beam splitter and focused in the nonlinear crystal at a shallow angle by a lens or a gold off-axis parabolic mirror. For routine

measurements, a 0.3 mm BBO crystal cut for type I phase matching was used as the nonlinear medium. In the interferometric configuration Si and InGaAs photodiodes were also used as nonlinear elements for autocorrelation measurements around 1300 and 2100 nm, respectively [88]. The path length of one arm was scanned by a translation stage with a motorized micrometer (DC Encoder Micrometer, Oriel). The signal from the detector was acquired with a box-car integrator (SR250, SRS) and computer acquisition card (PCI-6025E, National Instruments). Fig. 3.11 shows a schematic of interferometric (a) and intensity (b) autocorrelator configurations and typical autocorrelation traces of the Spitfire pulses obtained in each configuration.

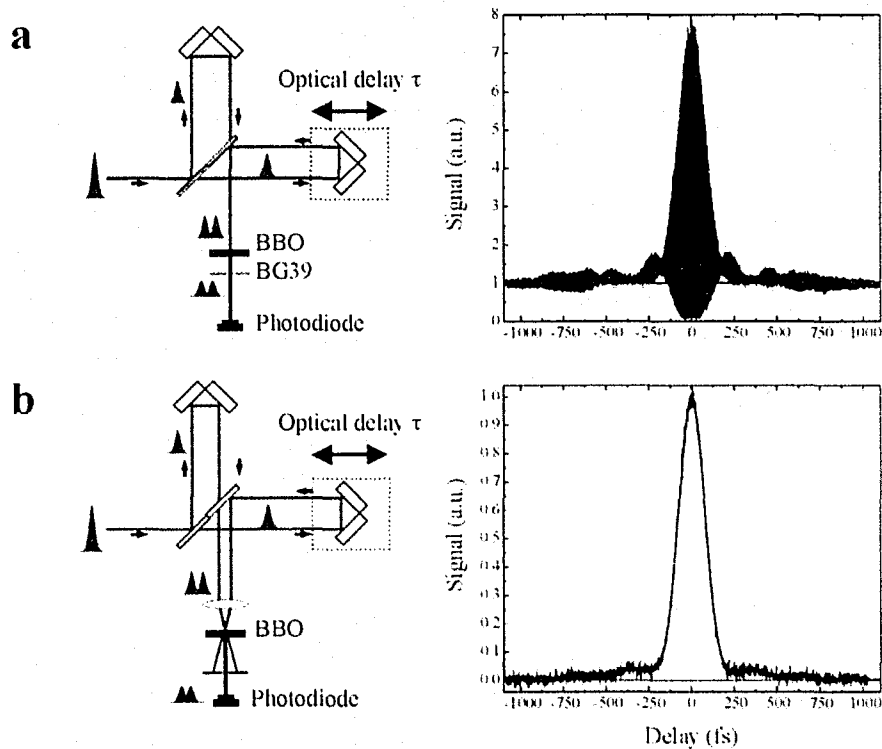


Figure 3.11: Schematic of (a) an interferometric and (b) intensity autocorrelator geometry along with typical autocorrelation traces of 130 fs Spitfire beam.

A second harmonic frequency resolved optical gating technique (SH-FROG) was used for more detailed pulse characterization. The configuration of this instrument is identical to that of an intensity autocorrelator shown Fig. 3.11(b) with the photodiode replaced by a fiber coupled spectrometer (PC2000, Ocean Optics). During a scan, a spectrum is recorded at each delay step forming a two-dimensional map of second harmonic wavelength vs. delay. A commercial inversion algorithm (Femtosoft Technologies) was used to retrieve the pulse shape. A typical SH-FROG trace and the retrieved pulse shape are shown in Fig. 3.12.

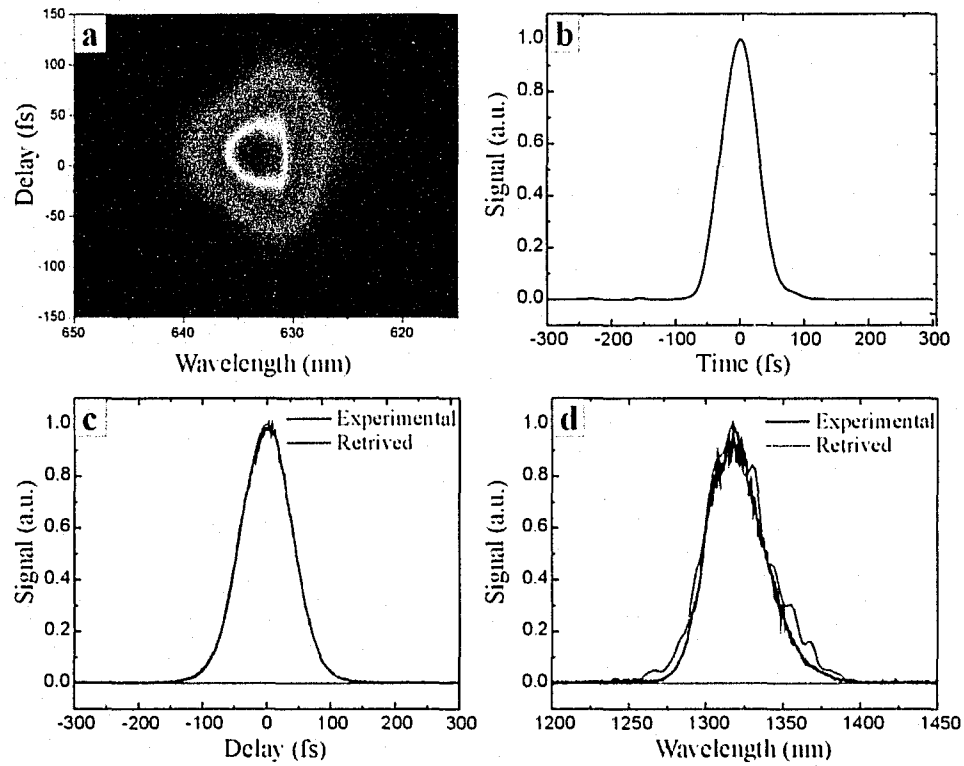


Figure 3.12: Second harmonic frequency resolved optical gating (SH-FROG) analysis of OPA signal beam centered around 1300 nm (a) SH-FROG trace, (b) temporal pulse shape retrieved, (c) intensity autocorrelation calculated based on the retrieved pulse shape (red) and measured independently (black), (d) signal spectrum of the pulse retrieved from the FROG trace (blue) and measured independently (black).

In several experiments utilizing pulses from an unseeded Spitfire cavity, the pulse duration was measured with a fast Si PIN photodiode (DET210, ThorLabs) with a 1 ns rise time. The pulse shape was recorded with a 400 MHz oscilloscope (TDS 3032B, Tektronix). Fig. 3.13 shows the pulse shape from the unseeded Spitfire cavity and the impulse response of the photodiode detector.

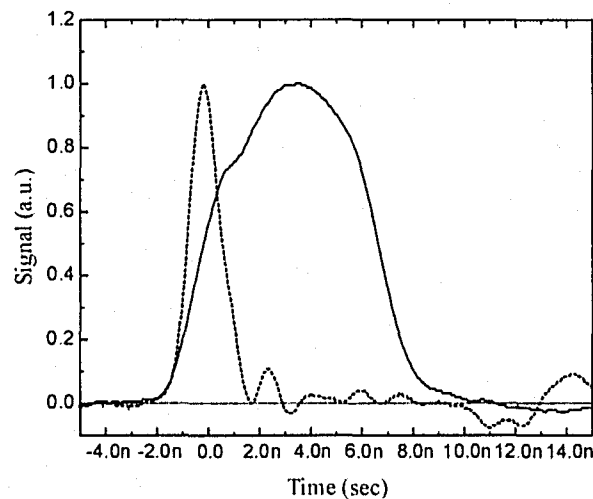


Figure 3.13: Pulse width measurement of an unseeded Spitfire amplifier. The impulse response of the detector is shown as a dashed line trace.

3.4.7 Single and Multiple Pulse Ablation Experiments

In experiments dealing with single and multiple pulse ablation, it was necessary to select a known number of pulses from the 1 kHz pulse train. The number of pulses delivered can be controlled in a several ways, for example, by using a combination of a Pockels cell and a polarizer; a fast mechanical shutter with minimum exposure time less than 1 ms; or by reducing the repetition rate of the amplifier to 100 or 10 Hz and using a slower mechanical shutter. Initially, the last method was adapted as it is the easiest and, by far, the least expensive. However, reducing the repetition rate of the amplifier to 10 Hz changes the thermal loading of the amplifier and leads to a decrease in the output pulse energy. A decrease of pulse energy in the range of few percent was not problematic in experiments utilizing pulses from the Spitfire LCX amplifier. The change in steady state conditions of the sub-50 fs Spitfire was a greater concern since that system was used to pump the OPA. The OPA is very sensitive to laser intensity fluctuations since it relies on nonlinear processes for wavelength conversion. A decrease of the OPA pump pulse energy by a few percent translated into a decrease in the OPA output pulse energy by as much as 50%. To avoid problems associated with changing the steady state condition of the laser caused by reducing the repetition rate, the repetition rate was decreased by using a phase locked optical chopper. The optical chopper (MC1000, ThorLabs) with a 10 slot wheel was phase locked to a sub-harmonic of the amplifier repetition rate yielding a 500 Hz pulse train. Blocking 9 out of 10 slots in the chopper wheel further reduced the repetition rate to 50 Hz allowing for the use of a slower mechanical shutter, while maintaining 1 kHz amplifier operation.

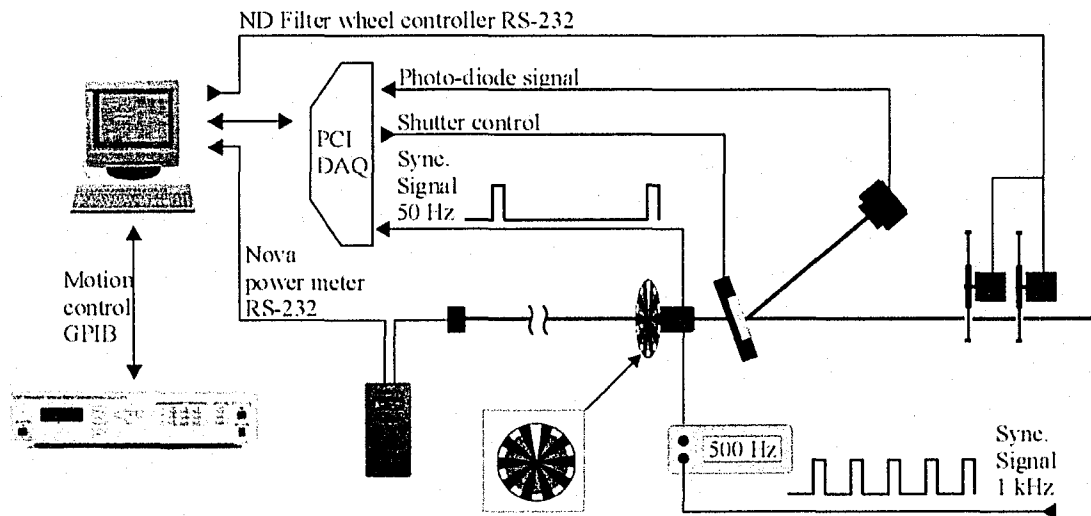


Figure 3.14: Detailed schematic of synchronization and acquisition.

With the pulse repetition rate reduced to 50 Hz, the single pulse ablation experiments were performed as follows:

- After the single pulse routine was initiated, the computer was armed and waited for the trigger from the chopper controller.
- Following the trigger pulse, the voltage reading from the photodiode was acquired, recorded and the shutter was opened for 20 ms, allowing 1 pulse to reach the sample.
- The translation stage was moved to the new position by a specified step size, the filter wheel was advanced to the next position and the process was repeated until a specified number of craters were produced.
- The log file containing a voltage reading at each filter wheel setting was recorded for each run.

3.4.8 Scribing and Groove Cutting Experiments

In the experiments involving groove cutting the individual pulse energy measurements were not required. Instead, the average power was measured with the power meter at all filter wheel settings prior to the experiments. Three basic types of experiments were routinely performed involving characterization of the groove depth as a function of the pulse energy, the feed rate and the number of consecutive passes over the same area. The sequence of these experiments was as follows:

- After one of the routines was initiated, a groove of specified length was cut by translating the sample relative to the stationary beam at a specified feed rate between 50 to 1000 $\mu\text{m/s}$.
- The sample was then moved to a new position, the filter wheel was advanced to a new setting and the process was repeated until a specified number of grooves was cut.

3.5 Analytical Tools

3.5.1 Scanning Electron Microscope (SEM)

The SEM was the primary tool used for post mortem sample analysis to assess surface morphology, lateral dimensions of ablation features and the depth of the grooves viewed in cross-section. All SEM analysis was performed with the SEM 515 (Philips). In most cases, the accelerating voltage was set to 20 kV and the measurements were made at magnifications between 1000 and 20000 times at tilt angles from 0 – 30°. The subjective and instrumental uncertainties in measurements were estimated by analysis of the calibration sample provided by the manufacturer. The horizontal and vertical dimensions of the calibration sample were measured several times, the sample was then rotated by 90° about axis normal to the surface, and the measurements were repeated. The variation between the measured dimension and the nominal dimensions provided by the manufacturer was always better than $\pm 5\%$.

During any given SEM session there are number of simple checks that can be performed to ensure that the magnification of the computer acquisition system is properly calibrated, for example, measuring the known spacing between laser machined features. Sample manipulation stages allow positioning of the samples with sub-micron resolution, therefore, inconsistencies in feature spacing measurement can alert the user of potential calibration problems.

3.5.2 Atomic Force Microscope (AFM)

The AFM was used primarily in the analysis of single pulse ablation craters presented in Section 4.3. Due to high lateral and vertical accuracy, the AFM is well suited for characterization of very shallow features and allows measurement of crater depths and volumes. The disadvantages of AFM include low dynamic range, typically less than 2 μm , and a scan area limited to 150 x 150 μm^2 . The AFM scans are also time consuming and therefore costly. All AFM scans were performed with a Nanoscope IIIa – multimode (Digital Instruments) operated in contact mode. AFM data analysis was performed with the Nanoscope software version 5.12. The software allows the user to examine collected data off-line and measure the lateral and vertical features as well as make volume measurements below or above specified planes. The same data sets were analyzed several times, a few weeks apart, to estimate the subjective uncertainty in measurements. The AFM data files were also exported in ASCII format and analyzed in MathCAD 2000. The variation in the lateral and crater depth measurements in all trials were typically less than $\pm 2\%$, while the variations in the volume measurements were typically less than $\pm 10\%$.

3.5.3 Optical Microscope (OM)

The OM was mostly used for preliminary assessment of the sample quality and in few cases for measurement of the lateral dimensions of the ablation craters. The resolution of the OM is approximately 0.5 μm and since most of the ablation features

were less than 10 μm , SEM was the primary measurement instrument. However, the OM is very sensitive to changes in surface reflectivity induced by laser irradiation. For example, the melted zone seen in Fig. 3.7 is very difficult to observe under SEM or even AFM due to very small depth changes in this region.

All OM measurements were performed with the Axioplan 2 (Zeiss) microscope operated in the differential interference contrast mode (DIC). In most cases, the samples were imaged with a 100 $\times$ objective and images were acquired with a digital camera. The calibration of the image acquisition and analysis software was performed by imaging a calibration sample provided by the manufacturer.

In a number of experiments, the lateral dimensions of single pulse ablation craters were measured with SEM, AFM and OM to compare the precision of the three instruments. The variation in lateral measurements performed by three instruments was less than $\pm 3\%$.

3.5.4 Transmission Electron Microscopy (TEM)

TEM is the most powerful analytical technique as it allows direct observation of microstructure and analysis of the chemical composition of the material with a resolution on the order of a few nanometers. A Philips CM12 conventional transmission electron microscope, operated at 120 kV, was employed for standard bright and dark field imaging of the shape and size of the single pulse ablation craters and the structure of the resolidified material. Standard selected area diffraction and convergent beam electron diffraction were used to determine the crystallographic structures of the regions investigated. Chemical analysis was performed with a field emission gun scanning TEM, JEOL 2010F operated at 200 kV. The JEOL 2010F was equipped with an EDX-UTW Link ISIS system for analytical x-ray spectroscopy and Gatan 666 electron energy loss spectrometer (EELS). Recently the microscope was upgraded to INCA analysis software and Gatan imaging filter (GIF). Both plan-view and cross sectional studies were prepared. Plan-view specimens suitable for TEM studies were prepared using the standard preparation techniques of mechanical back-thinning followed by argon ion beam milling until electron transparency was achieved. The cross sectional TEM samples were prepared by the focused ion beam (FIB) as described in Ref. 89. The specimens, coated with a protective tungsten layer, were milled using 50 keV Ga atoms. The "lift-out" technique was employed whereby the electron transparent foil was cut free by the FIB for stand-alone examination.

3.5.5 Degree of Polarization Technique (DOP)

Degree of polarization allows analysis of residual strain fields in the III-V semiconductors. The method of strain measurements using the degree of polarization technique is based on an analysis of the polarization state of a luminescent signal. The details of the technique can be found elsewhere [90,91]. Briefly, a low power 633 nm helium-neon laser beam is reflected from a cold mirror and focused on the sample facet by a 40 $\times$ microscope objective. The luminescence is collected with the same objective in a confocal arrangement and passes through the cold mirror, a filter which removes

residual HeNe light, and finally through a polarizer. The polarizer is continuously rotated with the rotation synchronized with the detection system such that signals L_x , and L_y , as well as L_{xy} , and L_{-xy} can be recorded. The schematic of the imaging setup is shown in Fig. 3.15.

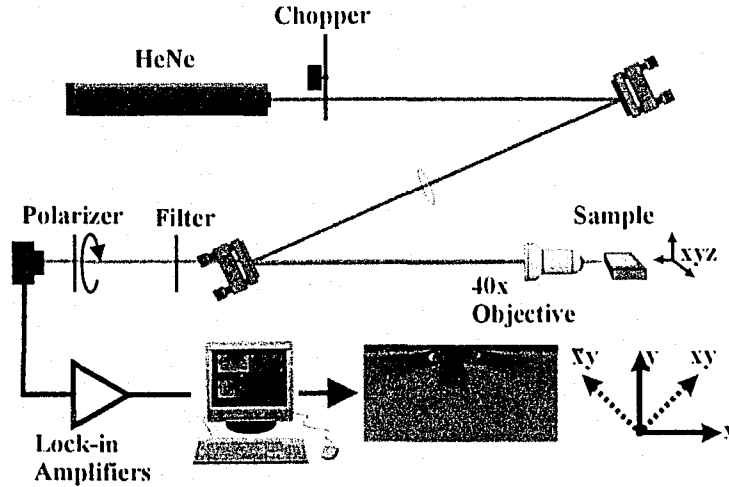


Figure 3.15: Schematic of DOP imaging setup.

The DOP signal is related to the luminescence signals measured in the two orthogonal polarizations (L_x , L_y) by

$$\rho_{DOP} = \frac{L_x - L_y}{L_x + L_y} = K_e (\epsilon_{xx} - \epsilon_{yy}) \quad (3.3)$$

where K_e is a calibration constant ($-9.4 \pm 0.1 \cdot 10^{-11} \text{ cm}^2 \cdot \text{dyn}^{-1}$ for InP) and ϵ_{xx} and ϵ_{yy} are the strains in the x and y directions [90]. The ROP (rotated degree of polarization) signal is related to the luminescence signals in the two orthogonal polarizations (L_{xy} , L_{-xy}) by

$$\rho_{ROP} = \frac{L_{xy} - L_{-xy}}{L_{xy} + L_{-xy}} = 2 \cdot K_e \epsilon_{xy} \quad (3.4)$$

where ϵ_{xy} are the shear strains. Two-dimensional images are obtained by scanning the sample past the stationary objective under computer control. At each point, values of L_x , L_y and L_{xy} , L_{-xy} are recorded and values of the DOP and ROP signals are calculated according to Eqs. (3.3) and (3.4) respectively. A strain resolution of $>10^{-5}$ and a spatial resolution of $\approx 1 \text{ } \mu\text{m}$ have been demonstrated [90].

Chapter 4

Single and Multiple Pulse Ablation

4.1 Introduction

This chapter is based on two previously published papers, and one manuscript accepted for publication. The papers describe the experimental results of single and multiple pulse ablation of InP. The work reported addresses more fundamental aspects of the ablation process. The reprints of the contributions are preceded by a short introduction outlining the key contribution to the field and acknowledgements specific to each paper. The comments on each set of experiments with possibilities for extension of the research are included at the end of each section.

4.2 Paper 1 - Femtosecond Laser Pulse Ablation of GaAs and InP: Studies Utilizing Scanning and Transmission Electron Microscopy

This paper presents the results of plan-view TEM studies of single pulse ablation craters on InP and GaAs. It is the extension of the work published on plan-view TEM analysis of the ablation craters on Si [92] completed during my Masters Thesis. The key points of interest in these studies were: investigation of changes in the crystal structure, surface morphology, and possible crystal defects beneath the ablation craters. Prior to this investigation, the detailed analysis of the final state of the material, especially utilizing TEM technique, was generally lacking. This paper was complementary to the first single pulse femtosecond ablation experiments on InP reported by Bonse *et al.* [53]. The post mortem analysis results were discussed in the framework of the dynamic studies presented by several research groups, most notably von der Linde *et al.* [17,20].

I was primarily responsible for laser ablation work, data analysis and writing of parts of the manuscript. Large portion of this manuscript, especially the discussion section was written by Dr. Harold Haugen. Andy Duft prepared the plan view TEM sample and Dr. Maureen MacKenzie and Dr. George Weatherly carried out all of the TEM work.

Parts of this work were presented as a part of my Masters Thesis. However, several follow up studies, in particular the threshold measurements, and most of the work on the manuscript preparation were completed during my Ph. D. studies.

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Femtosecond laser pulse ablation of GaAs and InP: studies utilizing scanning and transmission electron microscopy

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ABSTRACT Single pulse laser ablation of GaAs and InP using 130 fs light pulses at ≈ 800 nm was studied with various techniques, in particular, scanning and transmission electron microscopies. The final state of the material near the laser-ablated region following femtosecond ablation was characterized in detail for selected laser fluences. Threshold ablation laser fluences were also obtained for both compounds.

PACS 61.80.Ba; 64.60.-i; 79.20.Ds

1 Introduction

Materials processing has enormous technological importance and has been the subject of very extensive studies and developments over recent decades. Lasers have played an important role, and more recently, ultrashort pulse lasers in the femtosecond domain have offered unique advantages in this context. Ultrashort laser pulse ablation and machining has been studied for a wide range of materials, including semiconductors, metals, dielectrics and polymers (see e.g., [1–15]). In fact, femtosecond laser machining is often described as “damage free”. In order to understand the micro-modification (machining) process under normal operating conditions, the dynamics of single laser pulse ablation is investigated in detail. In the past few years a number of advanced studies have led to key insights into the dynamics of these ultrafast processes. These comprise impressive experiments on time-resolved microscopy, time-of-flight studies, and more recently, important developments in terms of X-ray based ultrafast analysis of the laser interaction processes [16–20]. This opens perspectives not only for a deep understanding of complex ultrafast laser-materials dynamics, but also prospects for novel materials modification on a micron or sub-micron length scale. Detailed investigations of the final state of the laser-ablated target material have generally been lacking. Thus extensive *ex situ* studies on the final state of the sample can provide important information complementary to the ultrafast dynamics

experiments. In the current work, we extend our recent experiments on single-shot laser ablation of silicon [21] to the compound semiconductors, GaAs and InP. Again, we employ pulse energies and tight focusing conditions which lead to ablation features on the few-micron scale. The effects of the ablation process on the structure and composition of the samples has been examined in detail. The properties of the solids were studied via a number of analytical techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), energy dispersive X-ray spectroscopy (EDX), and atomic force microscopy (AFM). Most notably, the TEM studies – the key thrust of the current work – provide new information on the nature of the ablated target material and the nature of the damage to the surrounding solid.

2 Experimental

The experimental approach has already been described in a separate paper concerning studies of silicon [21], but is briefly outlined here. An amplified Ti:sapphire laser with a wavelength of approximately 800 nm provided laser pulses of 130 fs duration. A fast mechanical shutter, synchronized with the laser, was used to control the number of pulses delivered to the sample from the (nominal) 1 kHz source. Laser pulse energies were adjusted with a set of thin reflective neutral density filters in steps of 0.1 OD ($\text{OD} = \log(I_0/I)$) over a pulse energy range of approximately 2 μJ to 10 nJ, but the typical laser pulse energies for in-depth transmission electron microscopy analysis were 18, 52 and 164 nJ for both GaAs and InP. (For purposes of comparison with other groups, the 164 nJ pulse energy utilized in the TEM study corresponds to a fluence of approximately 1000 mJ/cm^2 .) The laser beam was for most investigations focused on the sample by a 10 $\times$ microscope objective. A scanning knife edge technique determined a spot size ($2\sigma_{\text{th}}$) of 6.7 μm at the focus, and spot sizes were also obtained by measurements of crater size versus pulse energy. The (100) semiconductor samples were placed inside a small vacuum chamber mounted on a computer controlled xyz translation stage and machined under rough vacuum (~ 0.1 mbar). The laser beam was focused on the sample through a thin, uncoated sapphire window (200 μm thick) cut perpendicular to the *c*-axis.

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The post-irradiation surface morphology was first characterized by means of scanning electron microscopy. For selected samples, the crystal structure and composition in the vicinity of the ablation sites were investigated using transmission electron microscopy techniques, including energy dispersive X-ray spectroscopy and electron energy loss spectroscopy. For selected specimens, the depth and crater profiles were also measured with atomic force microscopy. Mechanical back-thinning followed by argon ion beam milling were used to prepare plan view specimens suitable for TEM investigations. The final sample often contained a hole surrounded by wedge-shaped electron transparent material. Analyses of the samples were performed using a variety of TEM techniques, including standard bright and dark field imaging approaches. The crystallographic structures of the regions investigated were determined through selected area diffraction and convergent beam electron diffraction. Since the preparation of high-quality TEM specimens is both challenging and time consuming for targets containing single-shot laser ablated spots on the micron scale, our TEM efforts were focused on three very different laser fluences for each material.

3 Results

Figure 1 shows a montage of SEM images of single shot ablation craters on InP, produced by pulses with pulse energies ranging from 24 nJ to 1 μ J. A very high degree of uniformity and reproducibility were achieved on the systematic irradiations of large-area wafer sections for SEM analysis. The features for GaAs were found to be quite similar to those depicted for InP. As with our study on Si [21] no abrupt changes in the surface features were observed with increasing pulse energy on either material. However, based on the observed surface morphology and debris patterns, three characteristic stages can be identified. Although the behaviour of the two compounds under laser irradiation was not identical, it is convenient to discuss the qualitative behaviour of both materials within the same pulse energy brackets. Stage 1 is

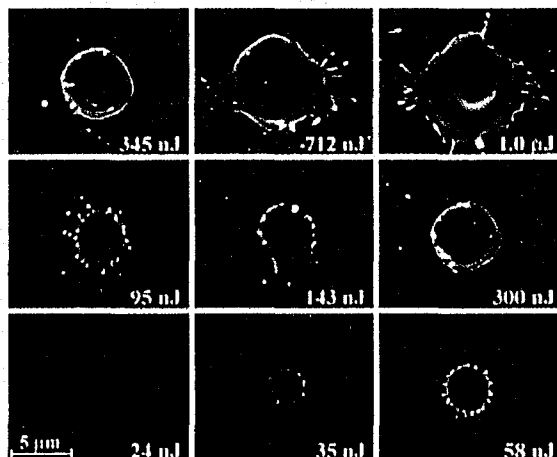


FIGURE 1 SEM images of single shot ablation craters on InP produced by 130 fs pulses with a range of energies

the near damage threshold regime and corresponds approximately to the energy range: $15 \text{ nJ} < E < 25 \text{ nJ}$; features are of the order of $1 \mu\text{m}$. (Unless otherwise stated, our damage thresholds are defined as some observable change in the sample surface observed under high resolution SEM.) In the second fluence bracket, corresponding approximately to the interval $25 \text{ nJ} < E < 150 \text{ nJ}$, a distinct circular rim forms around the craters. The third stage, $E > 150 \text{ nJ}$, corresponds to more violent expulsion of material from the crater resulting in randomly solidified material and deposition of droplets outside the crater region.

3.1 GaAs

Near the damage threshold the laser-modified areas were $\lesssim 2 \mu\text{m}$ in diameter and $< 50 \text{ nm}$ deep. Figure 2 presents TEM images and electron diffraction information from an affected region, as well as SEM pictures for a feature produced with an 18 nJ pulse. The feature is about $2 \mu\text{m}$ in diameter and has a surface texture within it of the order of $50\text{--}100 \text{ nm}$. The pronounced surface morphology of the affected area can be seen in Fig. 2 as a secondary electron image. The appearance of the affected area suggests the presence of a second phase but there was no evidence of this in the diffraction patterns, suggesting that it is a surface effect on top of a relatively large volume of unaffected substrate. EDX point analyses showed small changes in the Ga:As ratios in this region, suggesting that the surface layer may be Ga-rich.

In the intermediate pulse energy regime, the size of the craters increased up to almost $5 \mu\text{m}$. The rim, which marks the ablation edge, was not as clearly defined as in the case of single shot laser ablation of Si, and was typically between 75 and 100 nm high for pulse energies in this regime. Small polycrystalline droplets of GaAs $\approx 100 \text{ nm}$ in diameter were found

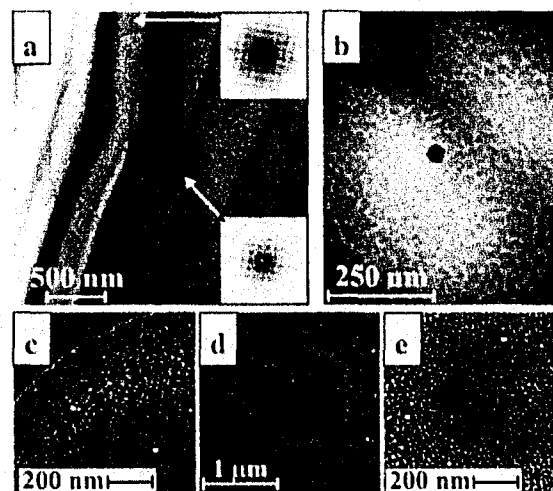


FIGURE 2 TEM and SEM images and diffraction patterns taken from an 18 nJ pulse crater on GaAs: a bright field TEM image with selected area diffraction patterns from the centre of the spot and the nearby substrate inset; b higher magnification bright field TEM image from centre of spot; c SEM image of edge of spot; d SEM image of spot; e SEM image of centre of spot

on the rim perimeter. Figure 3 contains a TEM image, electron diffraction information, and an SEM image from a crater produced by a 52 nJ pulse. The crater diameter is 2.5–3 μm and there is a pronounced rim of about 200 nm around the crater. The rim is essentially uniform. A surface morphology similar to that observed in the low power spot is found in the centre of the crater, although the distribution of globule sizes is somewhat different. This can be seen in the secondary electron image in Fig. 3, along with the morphology of the rim. Note that the affected area extends beyond the rim.

Pulses with energy of 164 nJ produced craters with a diameter of almost 5 μm , as shown in Fig. 4. The rims are about 200–300 nm wide and are polycrystalline, as illustrated by the diffraction pattern and dark field image, having a grain size up to about 50 nm. The grains on the inside of the rim appear to have a preferential orientation with their (111) planes aligned. Presumably during solidification their orientation was constrained by geometry to facilitate some form of epitaxy. The

rims are “splattered”, making them irregular in shape and they also contain a few defects. Droplets of gallium and a few defects were observed with the rim and a high density of defects was found in the centre of the craters. The corresponding secondary electron image is also shown in Fig. 4. Again, the same general surface morphology is observed, differing only in the globule size distribution.

3.2 InP

As for GaAs, near the damage threshold the affected areas were less than 2 μm in diameter and less than 50 nm deep. A typical laser-modified feature of $\approx 1 \mu\text{m}$ in diameter, resulting from an 18 nJ pulse, and corresponding diffraction patterns are shown in Fig. 5. Very little if any material has been expelled from the laser-irradiated spot but the material that has melted and resolidified is in the form of polycrystalline InP. The grain size is on the order of 5–20 nm and the grains were found to be randomly orientated.

The craters in the second fluence interval were typically between 2–5 μm in diameter with molten rims marking the boundaries of the craters. The rims were polycrystalline in nature and were between 50 and 120 nm in height. Droplets of single crystal In were also observed, many of which were found on the rims but also randomly distributed in and near the craters. A TEM image and diffraction pattern obtained with a 52 nJ laser pulse irradiation are shown in Fig. 6a, while an SEM image of a similar crater is shown in Fig. 6b. Our TEM analysis reveals the presence of polycrystalline InP in the cen-

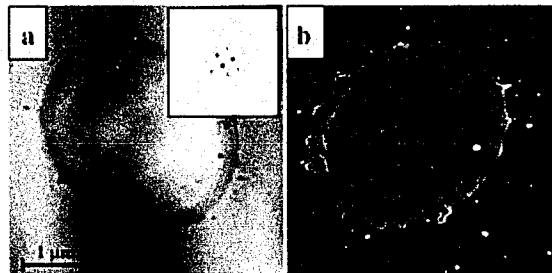


FIGURE 3 TEM and SEM images and diffraction patterns taken from a 52 nJ pulse crater on GaAs: a bright field TEM image with selected area diffraction pattern from spot and substrate; b SEM image of spot. Note that the affected area extends beyond the rim

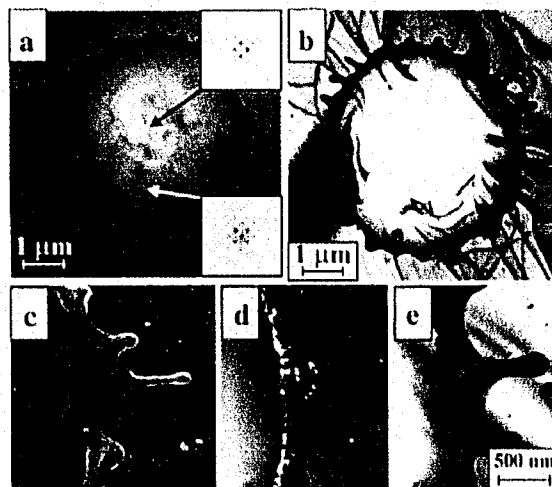


FIGURE 4 TEM and SEM images and diffraction patterns taken from 164 nJ pulse craters on GaAs: a bright field TEM image with selected area diffraction patterns from the centre of a laser-induced spot; b bright field TEM image of a crater; c SEM image of edge of a spot; d dark field TEM image of edge of a spot; e bright field image of edge of a spot

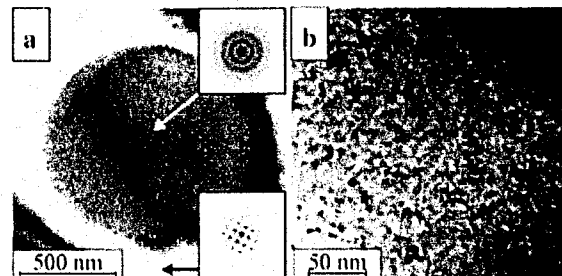


FIGURE 5 TEM image and diffraction patterns taken from an 18 nJ pulse crater on InP: a bright field TEM image with selected area diffraction patterns from the centre of the spot and the nearby solid; b higher magnification TEM image of centre of the spot showing polycrystalline nature of the grains

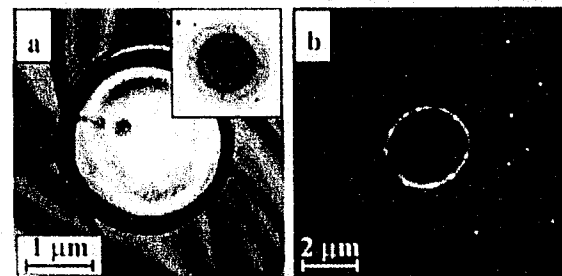


FIGURE 6 TEM image with diffraction pattern, and SEM image, taken from craters on InP: a bright field TEM image of a 52 nJ crater with diffraction pattern taken from the centre of the spot plus the surrounding material; b SEM image of a different feature from this fluence bracket

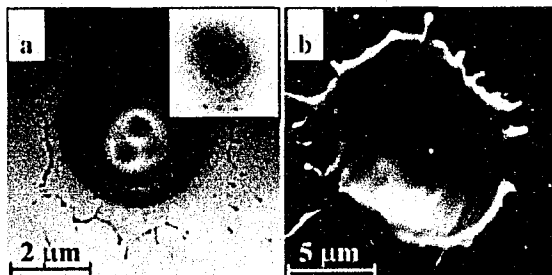


FIGURE 7 a Bright field TEM image from a 164 nJ pulse crater on InP; b SEM image of 400 nJ pulse crater on InP

tures of the craters as well as the underlying single crystal substrate. The 5–20 nm polycrystalline grains were distributed over the entire surface within the boundary of the rim.

Figure 7a shows a typical crater from the third fluence interval. It is about 4 μm in diameter and resulted from a 164 nJ pulse. As can be readily seen in the image, material was splattered out from the crater up to a distance of about 1 μm . The third ablation interval is reached much more quickly than in Si, and even more quickly than in GaAs. An increase in pulse energy above 200 nJ resulted in a significant amount of debris being deposited beyond the rim of the craters. At a pulse energy of 1.6 μJ the volume of displaced semiconductor was measured via AFM to be 17 μm^3 , but only 6 μm^3 of debris was found on the surface.

3.3 Threshold determinations

In order to augment our results on TEM analyses from irradiation at selected pulse energies, we subsequently conducted a series of D^2 back-extrapolation analyses on both InP and GaAs to obtain ablation threshold fluences [22]. Examples of our data from individual runs analyzed via SEM are illustrated in Fig. 8 for both compounds. For these plots, the size of the rims was measured as a function of laser pulse energy. These results were obtained with a 10 $\times$ microscope objective and for a wavelength of 800 nm. The results for the threshold fluences are $170 \pm 14 \text{ mJ/cm}^2$ and $226 \pm 20 \text{ mJ/cm}^2$ for InP and GaAs, respectively. For GaAs, only the result shown in Fig. 8 was obtained, while for InP, sets of measurements of crater sizes versus pulse energy were conducted through a series of separate runs. Table 1 summarizes the InP results for a variety of irradiation conditions where the data were taken on entirely separate runs. In view of the sensitivity of the back-extrapolation to errors in various parameters, there is a very good overall agreement amongst the data. A simple arithmetic average of the eight data sets for linearly polarized light in Table 1 yields a threshold of 160 mJ/cm^2 , in excellent agreement with the literature, as discussed further in Sect. 4. It should be noted that the back-extrapolation approach outlined above follows the evolution of a particular feature (the rim) as a function of laser pulse energy. We associate these obtained threshold values with ablation threshold fluences. However, some modification of the target can be expected at even lower fluences, as obtained with the smallest pulse energies used in this work.

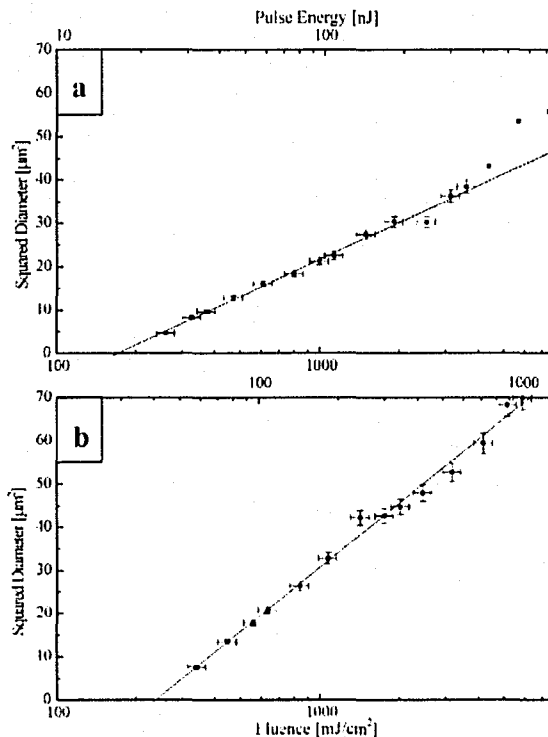


FIGURE 8 Examples of a D^2 back-extrapolation to obtain ablation threshold in a InP and b GaAs. Both results were obtained with a 10 $\times$ microscope objective and 800 nm light

Focusing Optic	Threshold Fluence * (mJ/cm^2)
75 millimeter plano-convex lens	154 ± 15
5 $\times$ microscope objective	154 ± 5
5 $\times$ microscope objective	164 ± 10
50 $\times$ microscope objective	133 ± 15
5 $\times$ microscope objective	145 ± 9
5 $\times$ microscope objective †	188 ± 12
10 $\times$ microscope objective	180 ± 15
10 $\times$ microscope objective	170 ± 14
5 $\times$ microscope objective	182 ± 12

* The uncertainties reflect solely the fitting routine, and do not incorporate other experimental errors. In particular, the fourth and fifth entries are expected to have additional errors due to the very tight focal region in the case of the 50 $\times$ objective and due to an additional pulse energy uncertainty for the fifth entry

† Obtained with circularly polarized light; other table entries use linear polarization

TABLE 1 Threshold fluence values for InP under various irradiation conditions for $\approx 800 \text{ nm}$, 130 fs pulse irradiation

4 Discussion

It is convenient to consider our results in the context of the work of von der Linde and co-workers. Cavalleri et al. [23] discuss the laser-solid interaction in terms of various fluence intervals, and provide key fluence values for both Si and GaAs under conditions of irradiation with 100 fs, 620 nm wavelength pulses. Initially (below 100 mJ/cm^2 in GaAs) energy is deposited but the sample does not melt. For lattice

temperatures exceeding 1513 K for GaAs (laser fluence of 100 mJ/cm^2), the sample melts in the near-surface region. Somewhat higher fluences cause melting via an ultrafast non-thermal process in GaAs. In fact, for GaAs, they found a well defined fluence threshold of 150 mJ/cm^2 for the boundary between the thermal and non-thermal melting regimes. Above an ablation threshold of 175 mJ/cm^2 in GaAs macroscopic amounts of material are ejected from the solid. The time-of-flight studies of [23] nicely illustrate an abrupt transition in the number of detected neutral atoms and ions at the ablation threshold. At somewhat higher fluences an interval can be defined which corresponds to material expansion without entering a two-phase regime. At still higher fluences, above 1 J/cm^2 (not considered in detail by Cavalleri et al. [23]), the threshold for plasma formation is reached. The highest pulse energy irradiations in our investigations fall into this last regime.

As outlined in Sect. 3, although no abrupt changes were observed in the behaviour of our irradiated samples as a function of laser fluence, there are three qualitative brackets that can be considered. Given the experimental uncertainties, the differences between GaAs and InP in this regard are sufficiently small to consider the brackets to be largely identical. For the bracket of $15 \text{ nJ} < E < 25 \text{ nJ}$, small features were observed on the surface via SEM. This is consistent with the melting regimes of Cavalleri et al., where small amounts of material would be affected. Our GaAs sample (under 18 nJ irradiation) showed only topographical changes near the damage threshold, while our InP sample exhibited fine-grained polycrystalline surface content after irradiation with the same pulse energy. In part, this could reflect the different material removal mechanisms for the two different compounds in this near-damage threshold fluence regime. However, it should also be noted that since both irradiations are close to the threshold for modification, the relative amount by which the individual irradiations exceed the threshold in the two cases can differ. (A discussion of the uncertainty in laser fluences is given below.) In the next bracket, $25 \text{ nJ} < E < 150 \text{ nJ}$, a distinct crater with a well-defined rim is formed, which is consistent with Cavalleri et al.'s ablation regimes. The rim was less pronounced around GaAs and InP craters than we observed earlier around Si craters. In addition, the surface quality of the GaAs and InP craters were similar, with evidence for polycrystalline material in both cases, but neither was equal in quality to Si craters formed via single pulse irradiation [21]. In addition, our work on Si(100) revealed single crystal craters. Nevertheless, in general, the craters were well defined and symmetric with no significant debris beyond the ablated area, until our third fluence interval was reached. In both binary compounds frozen liquid droplets on the order of 100 nm were found on the perimeter of the rim. With increasing pulse energy similar droplets were also found at the bottom of the craters. Finally, the region $E > 150 \text{ nJ}$, where there is violent expulsion of material, leads into the plasma regime. There was more evidence of violent expulsion of material at the lower fluences of the third fluence bracket for InP than for GaAs.

Long et al. [24] have reported laser-induced photochemical decomposition of GaAs(110) which was investigated via time-resolved photoelectron spectroscopy. A copper vapour laser providing 5 ns pulses at 510 nm was utilized in con-

junction with sub-nanosecond synchrotron radiation pulses. Under irradiation with multiple laser pulses at a repetition rate of 6 kHz , the formation of 15 nm sized Ga islands was obtained with individual pulse fluences as low as 1 mJ/cm^2 . Under single laser shot irradiation with our lower pulse energies, we observed a surface texture on the $50\text{--}100 \text{ nm}$ scale. Our EDX point analysis suggested a surface layer of Ga, in qualitative agreement with Long et al.

Bonse et al. [25] have made a detailed study of ultrashort pulse laser ablation of InP(100) in air, using 130 fs pulses at a wavelength of 800 nm . Much larger irradiation spots were utilized than in the present study. They employed optical microscopy, SEM, and Auger electron spectroscopy (AES) to study single and multiple shot irradiation of InP. The thresholds were determined by plotting the squared diameters [22, 25] of the craters versus laser fluence and extrapolating to zero. For single shot laser ablation they obtained a threshold of 160 mJ/cm^2 , in excellent agreement with our present study. Substantial incubation effects, as well as periodic surface structures, were found for multi-shot irradiation in their work. Their quantitative studies of crater depths were limited to irradiations of at least eight pulses due to the limited resolution of the optical microscope. Some discrepancies with their models are potentially attributed to effects of irradiation in air but the nonlinearity of the absorption process could also play a role. Their AES studies of chemical composition revealed In, P, O and C in all their spectra. They found the relative concentration of oxygen to increase in laser-irradiated regions, with evidence for both indium oxide and phosphorus oxide. Compositional changes between the various points in the craters were not observed with AES. Argument et al. [26] have also recently reported a damage threshold of 160 mJ/cm^2 for 130 fs duration pulses on InP at a wavelength of 800 nm , via a back-extrapolation of the squared diameter of ablation spots.

In addition to ultrafast laser ablation studies, there has also been recent interest in nanosecond laser patterning of InP via XeCl excimer lasers in the presence of a chlorine atmosphere (see e.g., [27, 28]). Prasad et al. [27] investigated surface patterning for optoelectronic device fabrication. They used a 10% gas mixture of chlorine diluted in helium and obtained a fluence threshold of 40 mJ/cm^2 for 308 nm light. Wrobel et al. [28] explored laser-assisted (308 nm) dry etching in low-pressure chlorine atmospheres at fluences lower than the ablation threshold of 140 mJ/cm^2 for InP. These chemically assisted dry etch schemes using nanosecond UV lasers offer an interesting, complementary approach to femtosecond laser micro-modification.

The uncertainties in the laser fluences for the selected samples utilized in the present TEM work is $\sim 50\%$ for the near-threshold values, due to the combined uncertainties in the focal spot determination, laser pulse energy, filling of the microscope objective, and the positioning of the target; and as regards the damage threshold, the difficulty of detecting the very small laser-induced spots. The uncertainty is expected to decrease somewhat at higher laser fluences. The relative consistency for a given set of data from the same run – where focal spot positioning, beam quality and alignment are expected to be more constant – should be better than comparisons between data taken at very different points in time. The thresholds ob-

tained from D^2 back-extrapolations for a broad range of crater sizes from samples prepared in more recent experiments, assuming a single dynamic regime, have a smaller uncertainty which we estimate to be around 15%. Our work typically utilizes much smaller focal spots than most other investigations, making the absolute fluence determinations particularly challenging. Moreover, our TEM data and SEM data for the D^2 back-extrapolations were taken months apart. Differences in laser conditions must also be considered in the comparisons between different groups, although, for example, laser wavelength differences are not as substantial as one might initially expect given the influence of nonlinear aspects of the laser-solid interaction. Nevertheless, our results are in very good qualitative and semi-quantitative agreement with the dynamical models of von der Linde and co-workers, and our InP ablation threshold obtained via a D^2 back-extrapolation is in excellent quantitative agreement with other literature values. We are also in good qualitative agreement with the ablation threshold obtained by Cavalleri et al. [23] for GaAs at a wavelength of 620 nm. They obtained 175 mJ/cm² for gallium arsenide, while our result is 226 mJ/cm² at 800 nm. Also, Huang et al. [29] studied the behaviour of the dielectric function of GaAs under intense ultrafast excitation. They utilized a 70 fs, 635 nm pump laser source to irradiate Cr-doped GaAs(100) samples below the damage threshold. Their damage threshold (100 mJ/cm²) was defined in terms of an observable change under an optical microscope. Our recent preliminary measurements using a high-resolution optical microscope have revealed modification thresholds for GaAs and InP of ~ 90 mJ/cm² and ~ 50 mJ/cm², respectively (130 fs pulses at 800 nm), assuming a typical (knife edge) spot size. Under conditions of 150 fs, 800 nm laser irradiation, Lindenberg et al. have reported a very low damage threshold of 15 mJ/cm² for the compound semiconductor InSb [19].

The area of ultrafast laser interactions has stimulated a great deal of theoretical interest. For example, Stampfli and Brenneemann [30] have analyzed the instabilities in both Si and GaAs introduced on a femtosecond time domain via intense laser irradiation. Their models are generally in good agreement with the experiments that explored the ultrafast dynamics. Graves and Allen [31] have used the method of tight binding electron-ion dynamics to study the response of GaAs to ultrafast and intense laser pulses. Through this approach they obtained a detailed microscopic understanding of the behaviour of both electrons and ions. Their predictions were consistent with various experiments including those by Mazur and co-workers [29], and von der Linde and collaborators [8]. Equations-of-state effects were discussed by Anisimov et al. [32], and Inogamov et al. have examined the models for the expansion of matter which is heated by an ultrashort light pulse [33]. Finally, we bring the reader's attention to a valuable overview of selected recent experiments and theoretical considerations, presented by von der Linde and Sokolowski-Tinten [34].

As discussed in our recent work on single femtosecond laser-pulse irradiation of Si(100) [21], it is rather surprising that we have not observed extended defects under detailed TEM observations in spite of the very large transient pressures predicted for the ablation process, on the order of tens of

GPa [35]. Under the assumption of an adequate coupling time in order to apply dislocation formation models [36], the pressure waves resulting from ultrafast laser ablation would exceed predicted critical pressures for the formation of extensive damage to the remaining solid. While the threshold for dislocation formation depends on the validity of certain assumptions [36], we would expect extended defects for pressures of a few GPa. Our evidence via electron microscopy is in qualitative agreement with the recent work employing time-resolved X-ray diffraction. Rousse et al. investigated non-thermal melting of InSb and found a maximum strain of 0.3% [16], while Rose-Petruck et al. reported a maximum strain of around 0.25% for GaAs [17]. Additional studies providing tests of the predictions of ultrafast dynamical models for structural details of the ablated material in the final state would be of considerable interest. We have also utilized a technique based on polarized photoluminescence for the analysis of optical quality of the resolidified material as well as the residual stress in the solid close to the ablated region [37]. Such studies are well suited to GaAs and InP.

5 Conclusions

The present investigation has provided detailed TEM-based studies of single-shot femtosecond laser irradiation of GaAs and InP for selected fluences, as well as a broader survey via SEM and AFM. The SEM and TEM observations provide information on both subtle and extensive surface modifications. Such input can be important for our understanding of the basic physical processes involved, as well as chemical and physical details of potential significance for various future applications. For example, the texturing of the near-surface region could have important implications for nano-technology areas. In contrast to the results obtained with longer laser pulses in the nanosecond regime, femtosecond laser-solid interactions are often described as "damage free". In this present investigation of single-shot femtosecond laser ablation of micron-sized areas on InP and GaAs, we have not observed extended defects with our detailed examinations for the three selected laser pulse energies using TEM techniques. The present study has concentrated on single shot laser irradiation effects. A natural extension of the work would be detailed TEM-based analyses of multi-shot irradiated samples. Finally, comparing the results of irradiation in air and in vacuum, particularly for the low fluence regime, as well as an extension of the work to a wide range of laser pulse lengths, would be of interest.

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REFERENCES

1. D. Bäuerle: *Laser Processing and Chemistry*, 3rd edn. (Springer Verlag, Berlin 2000), and references therein
2. K. Sokolowski-Tinten, H. Schulz, J. Bialkowski, D. von der Linde: *Appl. Phys. A* 53, 227 (1991)
3. X. Liu, D. Du, G. Mourou: *IEEE J. Quantum Electron.* QE-33, 1706 (1997)

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- 4 P.P. Pronko, S.K. Dutta, D. Du, R.K. Singh: *J. Appl. Phys.* **78**, 6233 (1995)
- 5 D. Ashkenasi, A. Rosenfeld, H. Rosenfeld, H. Varel, M. Wahmer, E.E.B. Campbell: *Appl. Surf. Sci.* **120**, 65 (1997)
- 6 H. Varel, D. Ashkenasi, A. Rosenfeld, M. Wahmer, E.E.B. Campbell: *Appl. Phys. A* **65**, 367 (1997)
- 7 S. Nolte, C. Momma, H. Jacobs, A. Tünnermann, B.N. Chichkov, B. Wellegehausen, H. Welling: *J. Opt. Soc. Am. B* **14**, 2716 (1997)
- 8 Sokolowski-Tinten, J. Bialkowski, D. von der Linde: *Phys. Rev. B* **51**, 14186 (1995)
- 9 X. Zhu, D.M. Villeneuve, A.Y. Naumov, S. Nikumb, P.B. Corkum: *Appl. Surf. Sci.* **152**, 138 (1999)
- 10 M. Lenzner, J. Krüger, W. Kautek, F. Krausz: *Appl. Phys. A* **69**, 465 (1999)
- 11 J. Bonse, S. Baudach, J. Krüger, W. Kautek, M. Lenzner: *Appl. Phys. A* **74**, 19 (2002)
- 12 S. Nolte, C. Momma, G. Kamlage, A. Ostendorf, C. Fallnich, F. von Alvensleben, H. Welling: *Appl. Phys. A* **68**, 563 (1999)
- 13 A. Cavalleri, K. Sokolowski-Tinten, J. Bialkowski, D. von der Linde: *Appl. Phys. Lett.* **72**, 2385 (1998)
- 14 C.B. Schaffer, A. Brodeur, J.F. Garcia, E. Mazur: *Opt. Lett.* **26**, 93 (2001)
- 15 K. Minoshima, A.M. Kowalevich, I. Hartl, E.P. Ippen, J.G. Fujimoto: *Opt. Lett.* **26**, 1516 (2001)
- 16 A. Rousse, C. Rischel, S. Fourmaux, I. Uschmann, S. Sebban, G. Grillon, P. Baleou, E. Förster, J.P. Geindre, P. Audebert, J.C. Gauthier, D. Hulin: *Nature* **410**, 65 (2001)
- 17 C. Rose-Petruck, R. Jimenez, T. Guo, A. Cavalleri, C.W. Siders, F. Ráksi, J.A. Squier, B.C. Walker, K.R. Wilson, C.P.J. Barty: *Nature* **398**, 310 (1999)
- 18 A. Cavalleri, C.W. Siders, F.L.H. Brown, D.M. Leitner, C. Tóth, J.A. Squier, C.P.J. Barty, K.R. Wilson, K. Sokolowski-Tinten, M. Horn von Hoegen, D. von der Linde, M. Kammler: *Phys. Rev. Lett.* **85**, 586 (2000)
- 19 A.M. Lindenberg, I. Kang, S.L. Johnson, T. Missalla, P.A. Heimann, Z. Chang, J. Larsson, P.H. Bucksbaum, H.C. Kapteyn, H.A. Padmore, R.W. Lee, J.S. Wark, R.W. Falcone: *Phys. Rev. Lett.* **84**, 111 (2000)
- 20 A. Cavalleri, C. Tóth, C.W. Siders, J.A. Squier, F. Ráksi, P. Forget, J.C. Kieffer: *Phys. Rev. Lett.* **87**, 237401 (2001)
- 21 A. Borowiec, M. MacKenzie, G.C. Weatherly, H.K. Haugen: *Appl. Phys. A* **76**, 201 (2003)
- 22 J.M. Liu: *Opt. Lett.* **7**, 196 (1982)
- 23 A. Cavalleri, K. Sokolowski-Tinten, J. Bialkowski, M. Schreiner, D. von der Linde: *J. Appl. Phys.* **85**, 3301 (1999)
- 24 J.P. Long, S.S. Goldenberg, M.N. Kabler: *Phys. Rev. Lett.* **68**, 1014 (1992)
- 25 J. Bonse, J.M. Wrobel, J. Krüger, W. Kautek: *Appl. Phys. A* **72**, 89 (2001)
- 26 M. Argument, S. Kirkwood, K. Chau, A. van Popta, Y. Tsui, R. Fedosejevs: *Tech. Digest SPIE: Proc. Opto-Canada TD01*, 196 (2002)
- 27 M. Prasad, H.E. Ruda, J.J. Dubowski: *J. Vac. Sci. Technol. B* **15**, 2046 (1997)
- 28 J.M. Wrobel, C.E. Moffitt, D.M. Wieliczka, J.J. Dubowski, J.W. Fraser: *Appl. Surf. Sci.* **127-129**, 805 (1998)
- 29 L. Huang, J.P. Callan, E.N. Glezer, E. Mazur: *Phys. Rev. Lett.* **80**, 185 (1998)
- 30 P. Stampfli, K.H. Bennemann: *Phys. Rev. B* **49**, 7299 (1994); P. Stampfli, K.H. Bennemann: *Appl. Phys. A* **60**, 191 (1995)
- 31 J.S. Graves, R.E. Allen: *Phys. Rev. B* **58**, 13627 (1998)
- 32 S.I. Anisimov, N.A. Inogamov, A.M. Oparin, B. Rethfeld, T. Yabe, M. Ogawa, V.E. Fortov: *Appl. Phys. A* **69**, 617 (1999)
- 33 N.A. Inogamov, Y.V. Petrov, S.I. Anisimov, A.M. Oparin, N.V. Shaposhnikov, D. von der Linde, J. Meyer-ter-Vehn: *JETP Lett.* **69**, 310 (1999)
- 34 D. von der Linde, K. Sokolowski-Tinten: *Appl. Surf. Sci.* **154**, 1 (2000)
- 35 K. Sokolowski-Tinten, J. Bialkowski, A. Cavalleri, D. von der Linde, A. Oparin, J. Meyer-ter-Vehn, S.I. Anisimov: *Phys. Rev. Lett.* **81**, 224 (1998)
- 36 A. Kelly, N.H. MacMillan: *Strong Solids*, 3rd edn. (Oxford Science Publications, New York 1986)
- 37 A. Borowiec, H.K. Haugen, D.M. Bruce, D.T. Cassidy: *Proc. CLEO* 2001, p. 517

The results presented are complementary to the detailed scanning probe microscopy and micro-Raman measurements of single pulse ablation craters on InP presented Bonse *et al.* [55,56]. However there are still some uncertainties as to the composition of the resolidified layer within the ablation craters. While micro-Raman measurements indicate that an amorphous phase of InP is present, this phase could not be positively identified with TEM. In plan-view TEM analysis it is difficult to detect an amorphous layer a few nanometers thick located on top of a substrate that is typically on the order of 100 nanometers. The diffraction patterns contain contributions from the resolidified layer and the underlying substrate. Furthermore, the plan-view TEM sample preparation involves mechanical grinding followed by the ion milling, which could lead to formation of an amorphous layer on the back side of the sample and further obstruct the signature of the amorphous layer inside of the crater.

Cross-sectional TEM is much better suited for the analysis of the microstructure of the resolidified layer. The advantage of cross-sectional TEM stems from the fact that the resolidified layer can be viewed directly without any background. The best approach would be a combined Raman and TEM investigation of the same crater. Comparing results prepared under different laser conditions could introduce additional uncertainty. For example, the work presented in this paper utilized tight focusing with a spot diameter $\sim 6\text{ }\mu\text{m}$ and irradiation of samples in rough vacuum, while all work presented by Bonse *et al.* involved irradiation in air with a spot diameter $\sim 46\text{ }\mu\text{m}$. The direct observation of the microstructure via cross sectional TEM would provide a valuable reference for Raman measurements, where the composition and structure of the material is deduced from the optical measurements.

Cross sectional TEM investigation of resolidified layer in Si ablation craters was recently presented by Jia *et al.* [93]. The studies presented in Ref. 93 complement our plan-view TEM analysis of single pulse ablation craters on Si [92]. Similar uncertainties, regarding the presence of an amorphous layer within the ablation crater, were raised in our experiments. The presence of an amorphous phase was unambiguously identified by Jia *et al.*[93] with the cross-sectional TEM technique, clearly demonstrating the advantages of this approach.

4.3 Paper 2 – Wavelength Dependence of the Single Pulse Femtosecond Ablation Threshold of Indium Phosphide in 400 – 2100 nm Range

This manuscript presents the systematic study of the wavelength dependence of the single pulse ablation threshold of InP. Prior to this work, all femtosecond laser ablation experiments on InP were performed with pulses centered at 800 nm. The use of the optical parametric amplifier and harmonic generation allowed us to access a broad range of wavelengths from 400 to 2100 nm. The key point of interest was comparison of the ablation threshold performed with pulses in the opaque and the transparent regions of InP.

The ablation threshold was determined based on the discontinuity in the maximum crater depth and equivalently discontinuity in the crater volume vs. fluence measurements. The crater measurements were performed with OM, SEM, and AFM. One drawback of AFM is the fact that the scans are time consuming and therefore costly. To reduce the scan time the craters were grouped in sets of five, scanned as a single image and analyzed separately afterwards. This approach allowed collection of large data sets in a relatively short time leading to substantially improved data statistics.

I would like to acknowledge Andy Duft, who performed all AFM scans, and very valuable discussions with Danny Perez, Patrick Lorazo, Dr. Lewis, Dr. Zhigilei and correspondence with Dr. Urbassek.

Wavelength Dependence of the Single Pulse Femtosecond Laser Ablation Threshold of Indium Phosphide in the 400 – 2050 nm Range

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Abstract

We present single-pulse femtosecond-laser ablation threshold measurements of InP obtained by optical, scanning electron, and atomic force microscopy. The experiments were conducted with laser pulses 65 – 175 fs in duration, in the wavelength range from 400 – 2050 nm, covering the photon energy region above and below the bandgap of InP. The ablation thresholds determined from depth and volume measurements varied from 87 mJ/cm² at 400 nm to 250 mJ/cm² at 2050 nm. In addition, crater depths and volumes were measured over a range of laser fluences extending well above the ablation threshold.

PACS: 79.20.Ds, 61.80.Ba

Keywords: Laser ablation, Femtosecond pulses, Indium phosphide

Introduction

Femtosecond laser ablation of semiconductors has been an area of intense fundamental and applied research for about two decades. A large amount of work has been reported on the study of dynamics and the analysis of the final state of the material [see, e.g., 1, 2, 3, 4, 5, 6, 7]. However the majority of femtosecond ablation studies on semiconductors published to date were performed with light pulses centered around the peak wavelengths of Ti:sapphire and dye lasers, ≈ 800 nm and ≈ 620 nm respectively. Analysis of the ablation of materials over a broader range of wavelengths can provide important information about the absorption processes and serve as experimental tests for advanced theoretical models. In this

work, we present systematic measurements of the wavelength dependence of the ablation threshold of InP in the range of 400 – 2050 nm, covering photon energies above and below the bandgap of InP, $E_g = 1.34$ eV, which corresponds to a wavelength of ≈ 925 nm. In addition, details on the crater dimensions were obtained for a wide range of laser pulse energies. The measurements were performed by optical microscopy (OM), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Experimental Setup

A commercial Ti:sapphire regenerative amplifier was used to produce pulses at ≈ 800 nm (Spectra-Physics, Spitfire LCX). Second harmonic beams at ≈ 400 nm were obtained by frequency doubling the fundamental beam in a

0.3 mm thick nonlinear optical crystal (BBO). Pulses in the near infrared (NIR) were obtained from an optical parametric amplifier (Spectra-Physics, OPA-800) pumped by another commercial Ti:sapphire regenerative amplifier (Spectra-Physics, sub-50 fs Spitfire). Typically the signal and idler beams were centered at wavelengths of 1330 and 2050 nm respectively. Finally the pulses at 660 nm were produced by frequency doubling the OPA signal beam in a 2 mm thick BBO crystal. The n-InP(100) samples were irradiated under a rough vacuum ~ 0.1 mbar base pressure. The laser was focused on the sample at normal incidence by a $5\times$ microscope objective. A set of thin, reflective neutral density filters was utilized to adjust the pulse energy on the sample. The pulse energy in the wavelength range of 400 - 1000 nm was measured with a semiconductor power meter (Ophir PD300-3W) while a surface absorbing head (Ophir 2A-SH) was used for power measurements at 1330 and 2050 nm. The experiments were conducted with femtosecond pulses of 65 - 175 fs in duration. The pulse duration at each wavelength was measured with a scanning, second order intensity autocorrelator and fitted to a Gaussian temporal profile. The pulse durations for each wavelength are given in Table 1. At each wavelength sets of craters produced by single pulses were prepared and analyzed by OM operated in the Nomarski mode. SEM, and AFM operated in the contact mode. Since AFM scans are very time consuming, craters were grouped in arrays of 5 (Fig. 1) and analyzed individually after the scan. Images of the sets of five craters contain 512×512 points. Several factors contribute to the uncertainties in the AFM measurements including calibration errors, the effects of finite pixel size, and the AFM tip geometry limitations in measuring sharp features.

Results

In the SEM and OM analysis the damage threshold and the spot size on the sample surface were obtained from measurements of the peak fluence dependence of crater diameters. Irradiation with pulse energies exceeding the modification threshold leads to the formation of several characteristic morphological regions, such as melting and ablation zones, rims, etc [6]. In all cases presented in this study the crater diameter was measured to the outside of the crater rim. This feature was most easily identified under all three microscopy techniques. The diameter D of each crater was measured as a function of pulse energy E by SEM, OM and AFM. By fitting the data to the equation

$$D^2 = 2\omega_0^2 \ln\left(\frac{E}{E_{th}}\right), \quad (1)$$

we obtain the Gaussian spot size ω_0 (beam radius measured at $1/e^2$), and the threshold energy E_{th} for crater formation [6,8]. Peak fluences are calculated with the equation

$$\phi_0 = \frac{2E}{\pi\omega_0^2}. \quad (2)$$

The maximum crater depth h_m was measured as a function of peak fluence ϕ_0 , and fitted to the logarithmic expression

$$h_m(\phi_0) = h_0 \ln\left(\frac{\phi_0}{\phi_{th}}\right), \quad (3)$$

where ϕ_{th} and h_0 are fit parameters. In the ablation of metals the parameter h_0 is often interpreted as an optical penetration depth in the low fluence regime.

The expression for the fluence dependence of the crater volume was derived following simple considerations analogous to those used to obtain Eq. 3 [9]. The fluence at radius r and depth h below the surface is given by

$$\phi(r, h) = (1 - R)\phi_0 \exp\left(\frac{-2r^2}{\omega_0^2} - \alpha h\right). \quad (4)$$

Assuming that the absorption coefficient α is constant and independent of intensity, the energy absorbed per unit volume is given by $-d\phi/dh = \alpha\phi$. If all material which receives an energy density in excess of H J/cm³ is ablated the crater profile $h(r)$ is defined by the condition $\alpha\phi(r, h) = H$ and yields

$$h(r, \phi_0) = \frac{1}{\alpha} \ln\left(\frac{\phi_0}{\phi_{th}}\right) - \frac{2r^2}{\alpha\omega_0^2} \quad \text{where } \phi_{th} = \frac{H}{\alpha(1-R)}. \quad (5)$$

The maximum crater radius r_m is found by setting $h(r_m, \phi_0) = 0$ and leads to an expression equivalent to Eq. 1. The ablated volume is given by

$$V(\phi_0) = 2\pi \int_0^{r_m} h(r, \phi_0) r dr = \frac{1}{2} \pi \left(\ln\left(\frac{\phi_0}{\phi_{th}}\right) \right)^2 \quad (6)$$

where $V_0 = \pi\omega_0^2/(4\alpha)$. This equation, based on very simple assumptions, provides the functional form for our data analysis. The crater volume V (the volume beneath the original surface), and the rim volume (the volume above the original surface), were measured as a function of peak fluence ϕ_0 and fitted to Eq. 6. In all cases the square root of volume was plotted as a function of $\log(\phi_0)$.

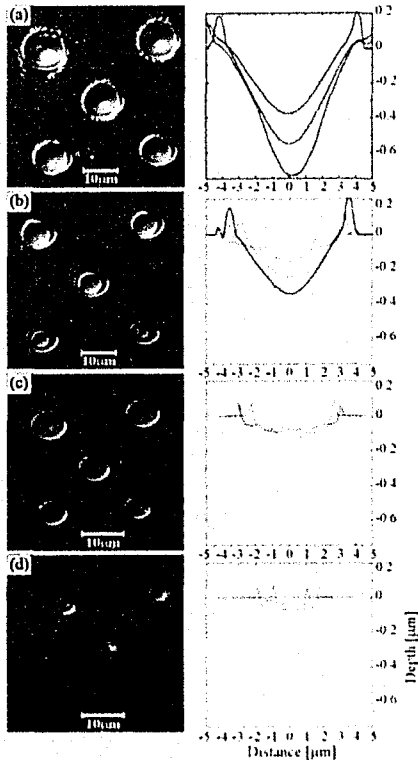


FIG. 1. (left) OM images of single pulse ablation craters produced by 105 fs, 660 nm pulses (right) AFM profiles of craters at upper left, center and lower right in each image, irradiated with fluences of (a) 4900, 3200, 2000 mJ/cm²; (b) 1700, 1100, 600 mJ/cm²; (c) 530, 390, 250 mJ/cm²; (d) 180, 120, 70 mJ/cm². Note that the images are not shown to the same scale. Please note the exaggerated z-axis in the crater profiles.

Fig. 1 (a-d) shows examples of OM images of ablation craters produced by irradiation with 660 nm pulses. The corresponding crater profiles for selected craters obtained from the AFM scans are shown on the right side of Fig. 1. Fig. 2 presents data collected for craters irradiated at a laser wavelength of 660 nm. Fig. 2(a) shows the D^2 measurements obtained by SEM, OM and AFM along with fits to Eq. 1. The spot size ω_0 was taken as the average value obtained from the three fits and used in all fluence calculations at a given wavelength. Fig. 2(b) shows the AFM measurements of the crater depth

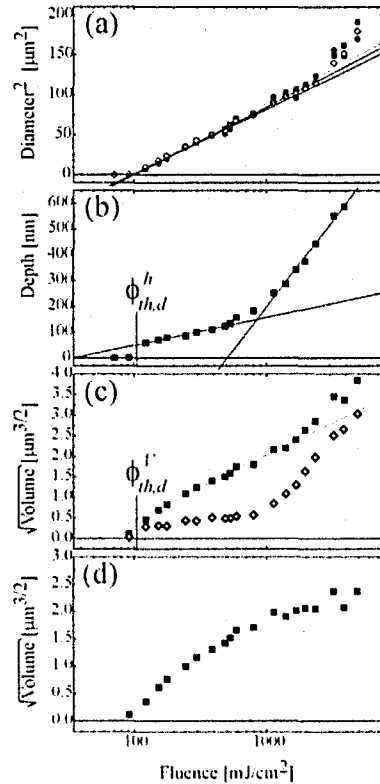


FIG. 2. Data analysis of single pulse ablation craters produced by 105 fs, 660 nm pulses showing (a) squared diameter measured by [■] SEM, [○] OM and [●] AFM, (b) crater depth, (c) square root of crater [■] and rim [○] volume, and (d) square root of the difference between crater and rim volume, plotted as a function of peak laser fluence.

dependence on fluence. Two distinct regimes, with different slopes and thresholds can be fitted to the data in the low ($\phi_a \leq 800$ mJ/cm²) and high ($\phi_a \geq 800$ mJ/cm²) fluence regions. The onset of the high fluence regime was taken as the intercept of the two fit lines in Fig. 2(b). At the other wavelengths, the high fluence regime onset varied from about 1000 to 3000 mJ/cm². The high fluence regime is characterized by a substantial increase in the slope of the depth vs. fluence for the ablation craters. The value of the fit parameter h_0 for the higher fluence regime is approximately 300 nm for all wavelengths in the opaque region, and 590 nm at a wavelength of 1300 nm. At 2050 nm the maximum pulse energy was insufficient to

investigate the high fluence regime. In the high fluence regime the crater profiles develop increased curvature (Fig 1(a,b)), and debris resembling resolidified liquid droplets is visible in the vicinity of some craters (Fig. 1(a)). Note the discontinuity in the crater depth data in the low fluence regime. We fit Eq. 3 only to the low fluence data points above the discontinuity. The parameters h_0 and ϕ_{th}^h thus obtained are considered simple numerical fit values. We take the fluence at the discontinuity as the effective depth ablation threshold. At fluences below this newly defined threshold $\phi_{th,d}^h$, surface modification was still evident, however, the loss of material was minimal with crater depths in the range of 1 – 3 nm. Fig. 2(c) shows the AFM measurements of the crater and the rim volume dependence on fluence. The straight line represents a fit to Eq. 6. As in the fluence dependence of the crater depth, the discontinuity in the crater volume data is observed in the low fluence regime, although it is not as pronounced. Similarly, the values of V_0 and ϕ_{th}^V obtained are considered numerical fit values. We take the fluence at the discontinuity as the effective volume ablation threshold $\phi_{th,d}^V$. Note that the fluence at the discontinuity of crater volume is the same as for the crater depth data. Two regimes analogous to those seen in Fig. 2(b) are clearly visible in the fluence dependence of the rim volume and to a lesser extent in the fluence dependence of the crater volume. Due to the AFM limitations in measuring droplets and other sharp features, the uncertainties in the rim volume measurements are expected to be substantially larger than for crater volume determination. Fig. 2(d) shows the plot of the difference between the crater and the rim volume.

The wavelength dependence of $\phi_{th,d}^h$ (or equivalently $\phi_{th,d}^V$) obtained from AFM measurements is shown in Fig. 3. Also, the average values, ϕ_{th}^D (avrg), obtained from a large number of SEM measurements performed over a course of several months are included in the same graph. The straight line represents a linear fit to the ϕ_{th}^D (avrg) data points at wavelengths of 400, 660 and 800 nm, including the origin. Fit parameters for AFM data are summarized in Table I. The superscripts h , V , and D are used to distinguish the respective fit parameter values. The uncertainty in the absolute threshold fluences is estimated to be about $\pm 25\%$, and is attributed to uncertainty in power and spot size measurements, as well as the fit uncertainties. The relative uncertainties for values

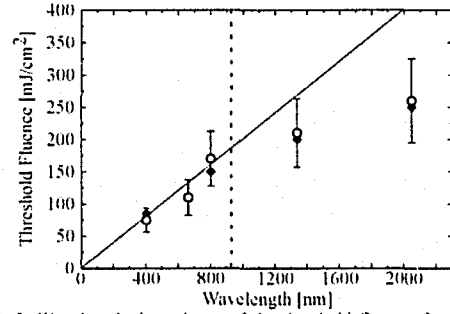


FIG. 3. Wavelength dependence of the threshold fluence for crater volume and crater depth $\phi_{th,d}^{h,V}$ (•) obtained from AFM data, and an average value of ϕ_{th}^D (avrg) obtained from a large set of SEM measurements (○). The solid line represents a linear fit to ϕ_{th}^D (avrg) for wavelengths below 925 nm. For clarity, only the error bars for ϕ_{th}^D (avrg) are shown. The vertical dashed line indicates the band gap of InP (1.34 eV). Laser pulse lengths are provided in Table I.

measured at different wavelengths are expected to be less than the absolute uncertainty.

TABLE I. Summary of fit parameters to Eqs. 1, 3 and 6 for the AFM data, depth and volume discontinuity values, and average values ϕ_{th}^D (avrg) obtained from a large set of SEM measurements. The pulse width measurements were performed with a second order interferometric autocorrelator. The depth and the volume thresholds were taken midway between the last point of shallow depth and the first point of substantial depth (volume), as shown in Fig. 2(b,c). The parameters h_0 and V_0 recorded in this table are given only for the low fluence regimes.

λ_0 nm	τ_p fs	ϕ_{th}^D mJ/cm²	ϕ_{th}^h mJ/cm²	ϕ_{th}^V (avrg) mJ/cm²	$\phi_{th,d}^{h,V}$ mJ/cm²	h_0 nm	V_0 μm³
400	~175	58	3.7	73	87	39	0.28
660	105	100	4.3	110	110	44	0.50
800	115	150	5.4	170	150	58	0.71
1330	65	210	6.3	210	200	61	1.4
2050	100	240	8.5	260	250	56	2.8

The AFM data provide additional information about the morphology and geometry of the ablation craters. Selected results of crater profiles obtained under 800 nm irradiation, as well as results for the depth versus fluence for all the laser wavelengths in the low fluence regime are illustrated in Fig. 4. The first two AFM profiles in Fig. 4(a) show the removal of a very small layer, and in the second case, just below the threshold $\phi_{th,d}^h$, a peak is clearly evident in the center. Upon surpassing the threshold (center, Fig 4(a)) the crater depth

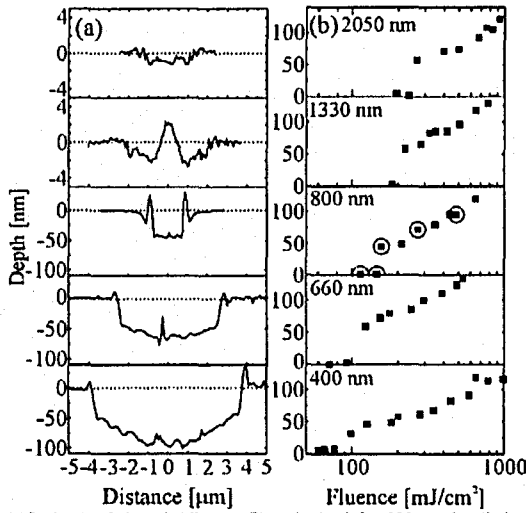


FIG. 4. (a) Selected AFM profiles obtained for 800 nm irradiation under the laser fluences of 110, 145, 155, 270 and 480 mJ/cm², highlighted in part (b) by open circles, and (b) crater depths versus laser fluence for various incident laser wavelengths. Note the large depth scale change in part (a) between the second and the third profiles, and the exaggerated depth scales in relation to the lateral dimensions.

becomes substantial, typically some tens of nanometers. The crater depth is fairly uniform in the lateral directions as seen in the crater profiles in Fig. 1(d) and the three highest fluences in Fig. 4(a). The profiles of craters in the low fluence regime clearly deviate from the shape predicted by Eq. 5.

With an increase of fluence above about 550 mJ/cm² (at 660 nm), a new surface morphological feature emerges in the center of the craters in Fig. 1(b). The inner feature is almost perfectly circular and is surrounded by a pronounced rim. This rim is significantly higher and thicker than the outer rim in the low fluence regime. The threshold fluence for emergence of this particular feature was estimated by D^2 fitting. The threshold fluence varied with wavelength from approximately 550 to 1300 mJ/cm², however there was no simple wavelength dependence. The effective spot size determined from the slope of the D^2 fit to the inner feature was 5.9 μm, whereas the spot size determined by a D^2 fit to the entire crater in the low fluence regime (Fig. 2 (a)) was 4.3 μm. At all wavelengths, a fit to the inner feature resulted in a larger spot size.

Discussion

The discontinuity in the fluence dependence of the crater depth and crater volume, hence the onset of significant material removal, was associated with the ablation threshold. The value of the ablation threshold of InP at 800 nm, $\Phi_{th,d}^{1,8} = 150$ mJ/cm², obtained from our AFM measurements is somewhat smaller than the value reported by Bonse *et al.* [6] who measured 230 mJ/cm². The apparent discrepancy might be a result of the different experimental conditions and the uncertainty in the respective fluence determinations by the two groups. All experiments presented in our study were conducted under rough vacuum and tight focusing (spot size of 5.4 μm at 800 nm), while experiments in Ref. [6] were conducted in air with spot size of 23 μm. A preliminary measurement performed in our laboratory under conditions similar to those in Ref. [6] yield an ablation threshold of 200 mJ/cm². This result suggests that different ambient atmosphere and focusing conditions might influence the ablation threshold. Previously [7,10] we have reported the ablation threshold of InP at 800 nm to be between 145-188 mJ/cm². However, these measurements were based on the D^2 fit only, using the outer edge of the rim. Other than our preliminary study [11], using solely D^2 analysis based on SEM measurements, the values of ablation threshold fluences of InP in the femtosecond regime at other wavelengths were not previously reported.

The present experiments were conducted with pulse durations in the 65 – 175 fs range (Table I). The dependence of the ablation thresholds on pulse length is known to be very weak for modest changes in pulse duration. Considering measurements presented in Refs. [5,12,13,14], if 100 fs pulse durations were used at all wavelengths, we could expect a ~10-20% increase in threshold at 1330 nm, and a similar or somewhat smaller threshold decrease at 400 nm and 800 nm. Based on our current data at five wavelengths (Fig. 3) it is difficult to say if the ablation threshold is a smooth, continuous function of wavelength or if it consists of two straight-line regions with different slopes. Two straight-line fits in respectively, the opaque and transparency regions, would cross in the close vicinity of the bandgap wavelength of InP. Clearly more data is required to determine if the bandgap energy constitutes a break point in the wavelength dependence.

Recently, damage threshold measurements for Si were reported [15] in a range from 780 nm in the

absorbing region, to 2200 nm wavelength in the transparency region of the spectrum. An increase of the damage threshold with wavelength was observed, ranging from about 300 mJ/cm² at 800 nm to 800 mJ/cm² at 2200 nm. The silicon results are qualitatively consistent with our findings for InP. The wavelength dependence of the ablation threshold was addressed by Gamaly *et al.* [16] who derived simple analytical expressions for the theoretical values of the ablation threshold for metals and dielectrics. Their two expressions predict linear dependences of the ablation threshold on the laser wavelength. The theory was in good agreement with experimental results obtained by Perry *et al.* [17] on fused silica. Simanovskii *et al.* [18] have recently reported mid-infrared (4.7-7.8 μ m) optical breakdown measurements in narrow-bandgap (ZnS, ZnSe) and wide-bandgap (LiF, MgF₂, CaF₂, BaF₂) dielectrics. For the wide-bandgap dielectrics, they found a substantial decrease in the breakdown thresholds with increasing wavelength in the mid-infrared region, while corresponding values for the narrow-bandgap materials were essentially independent of wavelength. In the visible region, the threshold for wide-bandgap dielectrics increased with wavelength, while in the same region the values for ZnSe were largely independent of the wavelength.

The theoretical analysis of the wavelength dependence of the ablation threshold requires consideration of the absorption and transport processes. The absorption processes determine the "initial" density and the spatial profile of the excited carriers. The primary mechanisms for carrier generation and energy deposition in semiconductors are single and multi-photon excitation as well as free carrier absorption and impact ionization. Two-photon absorption is particularly important in irradiation with intense femtosecond pulses [19,20,21]. If the effects of free carriers are neglected, the effective absorption coefficient can be written as [21,22,23,24]: $\alpha_{eff} = \alpha_{lin} + \beta \cdot I_0(1-R)$, where α_{lin} and β are one and two-photon absorption coefficients, I_0 is the incident laser intensity, and R is the small signal reflectivity. In the presence of two-photon absorption the effective absorption coefficient increases and can lead to deposition of the energy over a significantly shorter distance. For example, using the optical constants of InP at 800 nm [25], $\beta \approx 90$ cm/GW [23,26], and $I_0 \approx 10^{12}$ W/cm², yields $\alpha_{eff}^{-1} \approx 100$ nm, which is smaller than linear optical penetration depth at 800 nm ($\alpha_{lin}^{-1} = 303$ nm [25]). Free carrier absorption under near-ablation-threshold fluences can be expected to

lead to characteristic depths of the same order as given above, and hence must be included in a quantitative analysis. In addition to optical absorption, the subsequent carrier dynamics will influence the ablation threshold [21,27]. For example, Bulgakova *et al.* [28] have recently treated electronic transport and its implications for ultrafast laser ablation in a wide range of material types. In particular, they point out the distinction of dielectrics versus metals and semiconductors in terms of the laser-induced charging under femtosecond laser irradiation of materials.

Several interesting morphological features were observed in the AFM analysis. A peak seen in Fig. 4(a) just below the ablation threshold can be related to melt flow as discussed by Bonse *et al.* [6] and Bennett *et al.* [29]. We observed similar features at other wavelengths near the ablation threshold. An important aspect of the AFM data is the pronounced discontinuity in the fluence dependence of the crater depth in the vicinity of the ablation threshold (Fig. 4). A sudden increase in the ablation rate just above threshold has been previously reported, for example, after single pulse ablation of GaAs [30]. The final state of the material follows the behavior expected on the basis of ultrafast time-resolved microscopy studies [31]. Hashida *et al.* [32] reported rather rapid changes in the ablation rate of copper near thresholds under multi-pulse irradiation conditions. In studies utilizing time of flight mass spectroscopy the threshold of ablation was characterized by a sharp increase in the number of detected particles [33,34]. Several theoretical investigations of laser induced melting and ablation have utilized molecular dynamic (MD) simulations [35,36,37,38,39]. Schäfer *et al.* [38] have studied the ultrafast laser ablation of metals using a hybrid approach involving MD and heat conduction. In their simulation they obtained an ablation rate which rose very rapidly when the ablation threshold was exceeded. This increase was attributed to a spallation process. Perez and Lewis utilized a two-dimensional MD model to study ablation mechanisms [39]. The authors identified several processes of material removal, including spallation, phase explosion, fragmentation and vaporization. The discontinuity in the fluence dependence of the crater depth near the ablation threshold was also attributed to ejection of material by spallation. Our results on InP are similar to those obtained via MD models; for example, see Fig. 21 in Ref. [39]. However, the model was not believed to adequately describe non-thermal melting of covalent solids. More recently the MD simulations of ablation processes in Si were presented [40]. The authors concluded that phase

explosion is the primary mode of femtosecond laser-based material removal in semiconductors at fluences close to the ablation threshold.

An inner surface feature, similar to that seen in Fig 1(b) for $\phi_0 \geq 550 \text{ mJ/cm}^2$, has previously been reported in femtosecond ablation of InP with 800 nm pulses [6]. The morphology and structure of this feature were studied by optical and micro-Raman spectroscopy, and the authors associated the formation of this feature with the recrystallization of the molten semiconductor. The threshold fluence, determined by D^2 fitting, was 1300 mJ/cm^2 . D^2 fitting of our data at 800 nm yields a threshold fluence for the inner feature of 770 mJ/cm^2 . The threshold values are in reasonable agreement, considering the experimental uncertainties and the different experimental conditions as discussed above. As noted in the results section, D^2 fitting of the inner feature gives a larger spot size than D^2 fitting to the outside crater diameter in the low fluence regime. This discrepancy is most likely a result of mass transport. As the fluence is increased, a significantly larger volume of material is melted. Tight focusing leads to steep temperature gradients in the lateral dimensions, and due to the possibility of hydrodynamic flow [29], the final surface morphology is not expected to be an accurate representation of the local fluence.

The existence of low and high fluence ablation regimes has previously been reported in femtosecond laser ablation of metals [41,42,43], ceramics [44,45], and semiconductors [10,46, 47]. For example, in our earlier work on the micromachining of grooves in InP with 800 nm laser pulses [10], fit parameters were obtained for two ablation regimes, and the onset of the high fluence regime was apparent for values $\sim 1000 \text{ mJ/cm}^2$. However, the previous studies were based on multiple pulse irradiation, while the results presented in this study indicate that the two ablation regimes are also observed with single pulse irradiation. Although the current evidence is not generally as compelling as observed in the machining of grooves, it seems to rule out the cumulative effects, which play an important role in multiple pulse ablation [46,48]. Ablation in the second fluence regime was not studied in detail and the understanding of the underlying physics is still lacking. The two ablation regimes have been discussed for metals in the framework of the two-temperature model [41] where the final depth of the crater is related to characteristic depth of the energy deposition. According to the model the energy deposition profile in the low and the high fluence regimes is determined respectively by the optical

penetration depth and electronic heat conduction depth. For semiconductors, Bonse *et al.* [23] have reviewed multi-pulse data for ablation of Si and InP over a wide fluence range and suggested various physical mechanisms for the enhanced ablation yield at the higher fluences. It should be noted that our high fluence data reaches intensities associated with plasma formation [31,34,49]. Recently, Roeterdink *et al.* [49] presented the analysis of time of flight ablation of Si(111) (160 fs, 800 nm) in the fluence range $> 1000 \text{ mJ/cm}^2$. The authors presented experimental evidence of Coulomb explosion and plasma formation. In contrast, theoretical calculations and experimental results of other authors [28,50] suggest that Coulomb explosion only occurs in ablation of dielectrics. Discussions of the physics and experimental interpretations are on-going [51,52].

Summary

In summary, we presented the first detailed measurements of the wavelength dependence of the ablation threshold of InP over a wide photon energy range. Based on the discontinuity in the maximum crater depth (and equivalently the crater volume vs. fluence), the ablation threshold was found to vary from 87 mJ/cm^2 at 400 nm to 250 mJ/cm^2 at 2050 nm. This data can provide benchmarks for theoretical work aimed at predicting the wavelength dependence of the ablation threshold for compound semiconductors. A sharp discontinuity of the depth-versus-fluence behavior observed at all wavelengths is analogous to a number of other experimental results, and to recent results obtained from MD simulations showing spallation effects for femtosecond-laser irradiated materials. Finally, our results provide evidence for a two-regime description for the ablation of InP over a wide range of laser fluences.

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- [1] J. M. Liu, R. Yen, H. Kurz, N. Bloembergen, *Appl. Phys. Lett.* 39 (1981) 755.
- [2] C. V. Shank, R. Yen, C. Hirlimann, *Phys. Rev. Lett.* 51 (1983) 900.
- [3] J. Larsson, P. A. Heimann, A. M. Lindenberg, P. J. Schuck, P. H. Bucksbaum, R. W. Lee, H. A. Padmore, J. S. Wark, R. W. Falcone, *Appl. Phys. A* 66 (1998) 587.
- [4] D. von der Linde, K. Sokolowski-Tinten, *Appl. Surf. Sci.* 151-155 (2000) 1.
- [5] J. Bonse, S. Baudach, J. Krüger, W. Kautek, M. Lenzner, *Appl. Phys. A* 74 (2002) 19.
- [6] J. Bonse, J. M. Wrobel, K. -W. Brzezinka, N. Esser, W. Kautek, *Appl. Surf. Sci.* 202 (2002) 272.
- [7] A. Borowiec, M. MacKenzie, G. C. Weatherly, H. K. Haugen, *Appl. Phys. A* 76 (2003) 201; *Appl. Phys. A* 77 (2003) 411.
- [8] J. M. Liu, *Opt. Lett.* 7 (1982) 196.
- [9] D. Bäuerle, "Laser Processing and Chemistry" 3rd Edition, Springer-Verlag Berlin Heidelberg 2000.
- [10] A. Borowiec, H. K. Haugen, *Appl. Phys. A* 79 (2004) 521.
- [11] A. Borowiec, H. K. Haugen, paper CFF5, Conference on Lasers and Electrooptics (CLEO) 2003.
- [12] A. C. Tien, S. Backus, H. Kapteyn, M. Murnane, G. Mourou, *Phys. Rev. Lett.* 82 (1999) 3883.
- [13] H. O. Jeschke, M. E. Garcia, M. Lenzner, J. Bonse, J. Krüger, W. Kautek, *Appl. Surf. Sci.* 197-198 (2002) 839.
- [14] M. Lenzner, J. Krüger, S. Sartania, Z. Cheng, Ch. Spielmann, G. Mourou, W. Kautek, F. Krausz, *Phys. Rev. Lett.* 80 (1998) 4076.
- [15] H. Liu, G. Mourou, Y. N. Picard, S. M. Yalovsky, T. Juhasz, "Effects of Wavelength and Doping Concentration on Silicon Damage Threshold", CLEO/IQEC and PhAST Technical Digest on CD-ROM (The Optical Society of America, Washington, DC, 2004), CThD3.
- [16] E. G. Gamaly, A. V. Rode, B. Luther-Davies, V. T. Tikhonchuk, *Phys. of Plasmas* 9 (2002) 949.
- [17] M. D. Perry, B. C. Stuart, P. S. Banks, M. D. Feit, V. Yanovsky, A. M. Rubenchik, *J. Appl. Phys.* 85 (1999) 6803.
- [18] D. M. Simanovskii, H. A. Schwettman, H. Lee, A. J. Welch, *Phys. Rev. Lett.* 91 (2003) 107601.
- [19] A. Rousse, C. Rischel, S. Fourmaux, I. Uschmann, S. Sebban, G. Grillon, Ph. Balcou, F. Förster, J. P. Geindre, P. Audebert, J. C. Gauthier, D. Hulin, *Nature* 410 (2001) 65.
- [20] D. H. Reitze, T. R. Zhang, W. M. Wood, M. C. Downer, *J. Opt. Soc. Am. B* 7 (1990) 84.
- [21] K. Sokolowski-Tinten, D. von der Linde, *Phys. Rev. B* 61 (2000) 2643.
- [22] W. Kautek, J. Krüger, *Mat. Sci. Forum* 173-174 (1995) 17.
- [23] J. Bonse, M. Lenzner, J. Krüger, *Recent Rev. Devel. Applied Phys.* 5 (2002) Part II, 437.
- [24] K. Sokolowski-Tinten, J. Bialkowski, D. von der Linde, *Phys. Rev. B* 51 (1995) 14186.
- [25] E. D. Palik, "Handbook of Optical Constants of Solids", p. 511, Academic Press, San Diego, California 1985.
- [26] M. D. Dvorak, B. L. Justus, *Optics Comm.* 114 (1995) 147.
- [27] I. Sjodin, H. Petek, H. -L. Dai, *Phys. Rev. Lett.* 81 (1998) 5664.
- [28] N. M. Bulgakova, R. Stönan, A. Rosenfeld, I. V. Hertel, E. E. B. Campbell, *Phys. Rev. B* 69 (2004) 051102.
- [29] T. D. Bennett, D. J. Krajnovich, C. P. Grigoropoulos, P. Baumgart, A. C. Tam, *J. Heat Transfer* 119 (1997) 589.
- [30] V. V. Tsemov, K. Sokolowski-Tinten, N. Stojanovic, S. Kudryashov, D. von der Linde, B. Kogan, A. Schlarb, B. Weyers, R. Möller, J. Seckamp, C. Sotomayor-Torres, *SPIE proc.* 4760 (2002) 1032.
- [31] K. Sokolowski-Tinten, J. Bialkowski, A. Cavalleri, D. von der Linde, A. Oparin, J. Meyer-ter-Vehn, S. I. Anisimov, *Phys. Rev. Lett.* 81 (1998) 224.
- [32] M. Hashida, A. F. Semerok, O. Gobert, G. Petite, Y. Izawa, J. F. Wagner, *Appl. Surf. Sci.* 197-198 (2002) 862.
- [33] A. Cavalleri, K. Sokolowski-Tinten, J. Bialkowski, D. von der Linde, *Appl. Phys. Lett.* 72 (1998) 2385.
- [34] A. Cavalleri, K. Sokolowski-Tinten, J. Bialkowski, M. Schreiner, D. von der Linde, *J. Appl. Phys.* 85 (1999) 3301.
- [35] D. S. Ivanov, L. V. Zhigilei, *Phys. Rev. Lett.* 91 (2003) 105701.
- [36] L. V. Zhigilei, B. J. Garrison, *J. Appl. Phys.* 88 (2000) 1281.
- [37] D. Perez, L. J. Lewis, *Phys. Rev. Lett.* 89 (2002) 255504.
- [38] C. Schäfer, H. M. Urbasek, L. V. Zhigilei, *Phys. Rev. B* 66 (2002) 115404.
- [39] D. Perez, L. J. Lewis, *Phys. Rev. B* 67 (2003) 184102.
- [40] P. Lorazo, L. J. Lewis, M. Meunier, *Phys. Rev. Lett.* 91 (2003) 225502.
- [41] S. Nolte, C. Momma, H. Jacobs, A. Tünnermann, B. N. Chichkov, B. Wellegehausen, H. Welling, *J. Opt. Soc. Am. B* 14 (1997) 2716.
- [42] K. Furusawa, K. Takahashi, H. Kumagai, K. Midorikawa, M. Obara, *Appl. Phys. A* 69 (1999) S359.
- [43] N. N. Nedialkov, S. E. Ivanova, P. A. Atanasov, *J. Phys. D* 37 (2004) 638.
- [44] Y. Hirayama, H. Yabe, M. Obara, *J. Appl. Phys.* 89 (2001) 2943.
- [45] Y. Hirayama, M. Obara, *J. Appl. Phys.* 90 (2001) 6447.
- [46] J. Bonse, J. M. Wrobel, J. Krüger, W. Kautek, *Appl. Phys. A* 72 (2001) 89.
- [47] N. Bärsch, K. Körber, A. Ostendorf, K. H. Jönshoff, *Appl. Phys. A* 77 (2003) 237.
- [48] Y. Jee, M. F. Becker, R. M. Walser, *J. Opt. Soc. Am. B* 5 (1988) 648.
- [49] W. G. Roeterdink, L. B. F. Juurlink, O. P. H. Vaughan, J. Dura Diez, M. Bonn, A. W. Kleyn, *Appl. Phys. Lett.* 82 (2003) 4190.
- [50] R. Stönan, A. Rosenfeld, D. Ashkenazi, I. V. Hertel, N. M. Bulgakova, E. E. B. Campbell, *Phys. Rev. Lett.* 88 (2002) 97603.
- [51] R. Stönan, A. Rosenfeld, I. V. Hertel, N. M. Bulgakova, E. E. B. Campbell, *Appl. Phys. Lett.* 85 (2004) 694.
- [52] W. G. Roeterdink, M. Bonn, A. W. Kleyn, *Appl. Phys. Lett.* 85 (2004) 696.

Although the investigation of the wavelength dependence of the ablation threshold was the main goal of this study, AFM data acquired contains more quantitative information about the ablation process. Several possibilities for further data analysis and experiments can be considered.

The functional dependence of the ablation threshold on wavelength requires further experimental and theoretical work. Experimentally it would be particularly interesting to extend the measurements to wavelengths in the mid infrared to better characterize the dependence of the ablation threshold in the transparent region of InP. A detailed theoretical treatment is required to gain a better understanding of the nonlinear absorption channels, the role of free carriers, carrier diffusion and energy transport prior to the ablation process. The knowledge of the absorption profile is necessary in calculations of the theoretical ablation threshold of the material and crater profiles.

4.4 Paper 3 – Subwavelength ripple formation on surfaces of compound semiconductors irradiated by femtosecond pulses

This paper presents studies of laser induced periodic surface structuring (LIPSS) on InP, InAs, GaAs, GaP, Si, Ge and sapphire after multiple pulse irradiation with femtosecond pulses centered at wavelengths of 800, 1300 and 2100 nm. In addition to classic LIPSS with a spatial period comparable to the laser wavelength additional periodic surface structures were observed with a spatial period 4.2 – 5.1 times smaller than the free space wavelength of the incident radiation. Conditions required for the formation of these high spatial frequency LIPSS (HSFL) were identified. The study was complementary to observations of similar patterns reported on dielectrics and ceramics after irradiation with femtosecond pulses [59 – 64].

I would like to acknowledge very useful discussions with Dr. J. S. Preston who suggested extension of the initial experiment on InP to Si in order to study the effects of lattice symmetry on formation of HSFL. I also would like to thank Dr. J. E. Sipe and Dr. J. F. Young for helpful comments.

Subwavelength ripple formation on the surfaces of compound semiconductors irradiated with femtosecond laser pulses

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High-spatial-frequency periodic structures on the surfaces of InP, GaP, and GaAs have been observed after multiple-pulse femtosecond laser irradiation at wavelengths in the transparency regions of the respective solids. The periods of the structures are substantially shorter than the wavelengths of the incident laser fields in the bulk materials. In contrast, high-frequency structures were not observed for laser photon energies above the band gaps of the target materials. © 2003 American Institute of Physics. [DOI: 10.1063/1.1586457]

Coherent surface structuring after laser irradiation of solids, also termed ripple formation, was first observed by Birnbaum¹ on various semiconductor surfaces. Since then, laser-induced periodic surface structures (LIPSS) have been reported on virtually all materials.^{2–12} In many cases, after irradiation at normal incidence, the period of the observed structures is close to the wavelength of the incident radiation, with ripples oriented perpendicular to the direction of the electric field. However, reports of periodic structure formation with spatial period much smaller than the laser wavelength have recently been published.^{13–15} Varel *et al.*¹³ presented images of ablation craters produced on sapphire under multiple-pulse irradiation conditions (200-fs, 790-nm pulses) where patterns resembling higher spatial frequency ripples can be seen in the annular region see Fig. 1(c) in Ref. 13). Ozkan *et al.*¹⁴ found ripples with periods ~50–100 nm resulting from 248-nm femtosecond laser irradiation of thin diamond films. Yasumaru *et al.*¹⁵ reported formation of ripple patterns with mean periods of 100–125 and 30–40 nm on TiN and diamond-like carbon after irradiation with 800- and 267-nm femtosecond pulses, respectively.

We have extended the scope of these investigations to other materials and laser wavelengths. Our laser-irradiation studies were performed on (100) InAs, InP, GaP, and Si with femtosecond pulses at wavelengths of 2100, 1300, and 800 nm, and selected experiments were also conducted on (111) Ge, (100) and (110) GaAs, and sapphire samples (cut perpendicular to the *c*-axis). Under specific conditions, we observed the formation of high-spatial-frequency LIPSS (HSFL) on InP, GaP, GaAs, and sapphire, where the period of the LIPSS is significantly smaller than the wavelength of the incident light. Classic low-spatial-frequency LIPSS (LSFL), with a spatial period close to the wavelength of the excitation pulse, were observed on all materials studied after irradiation with all three wavelengths.

A commercial 130-fs Ti:sapphire regenerative amplifier was used to produce pulses at 800 nm, while pulses in the near infrared were obtained from an optical parametric am-

plifier pumped by another commercial 50-fs Ti:sapphire regenerative amplifier. Signal and idler beams at center wavelengths of 1300 and 2100 nm, respectively, and having pulse durations of 50–100 fs, were used. The samples were placed inside a small vacuum chamber (~0.1 mbar base pressure) mounted on a precision, computer-controlled xyz translation stage. A manual rotation stage allowed positioning of the sample around an axis normal to the sample surface in studies of the dependence of LIPSS formation on the crystal orientation. In this work, the number of pulses delivered to the samples is limited to rather low values, typically 1–100. This was achieved via a fast mechanical shutter synchronized with the laser operating at 10 Hz. The linearly polarized laser beam was focused on the sample at normal incidence by a 5× microscope objective, yielding spot sizes (beam radius at $1/e^2$) on the sample surfaces of ~5 μm at 800 nm and ~7–10 μm at 1300 and 2100 nm. After irradiation, the surface morphology was examined under a scanning electron microscope (SEM).

Single-femtosecond pulses with fluence exceeding the ablation threshold were found to leave smooth craters on the surfaces, exhibiting a characteristic rim marking the ablated area, with no evidence of LIPSS. The periodic surface structuring appeared only after several consecutive pulses and was found to depend on the material, the laser pulse fluence, the total accumulated fluence, and the wavelength. As in previous studies,^{1–12} LSFL were most pronounced after multi-shot irradiation with single pulse fluences in the vicinity of the ablation threshold. In our experiments, HSFL were also observed, as illustrated for InP in Fig. 1. The figure shows the morphology of two ablation craters after irradiation with 20 pulses at a laser wavelength of 2100 nm, for single-pulse energies of 390 and 1100 nJ. The spatial period of HSFL is ~430 nm. The formation of HSFL on InP was observed only after irradiation with 1300- and 2100-nm pulses, wavelengths corresponding to photon energies below the band-gap energy of InP, and with pulse fluence below the single-pulse ablation threshold. At fluences above the single-pulse ablation threshold, following multiple-pulse irradiation, the dominant features were the LSFL [Fig. 1(b)], with spatial periods close to the free space wavelength of the excitation pulse.

Figure 2 presents HSFL and commonly observed LSFL.

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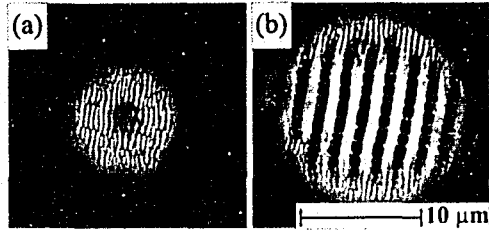


FIG. 1. Surface morphology of (100) InP after irradiation with 20 pulses at 2100 nm and pulse energies of (a) $E_p = 390$ nJ and (b) $E_p = 1100$ nJ. Ripples are perpendicular to the direction of the electric field. Some residual HSFL can still be seen on the outer perimeter of the larger feature, where the local fluence is below the single-pulse ablation threshold.

formed on GaP after irradiation with 800-, 1300-, and 2100-nm pulses. All three wavelengths are in the transparent region of GaP. The images were taken from central areas of the irradiated regions and were achieved under fluence conditions where respectively the HSFL and LSFL are the dominant structures. Figure 3 shows images of GaP, InP, InAs, and Si after irradiation with a 2100-nm beam, 20 consecutive pulses, and pulse fluences near the respective ablation thresholds. HSFL form rapidly in GaP and InP, appearing after a few consecutive laser pulses. In contrast with GaP and InP, which are both transparent at 2100 nm, no trace of HSFL was found on the surface of InAs, which is opaque at 2100 nm. Furthermore, no HSFL were revealed via SEM on Si (Fig. 3) under these conditions, nor at 2100 nm on a (111) Ge crystal, despite the fact that both are transparent at that wavelength. The spatial periods of LIPSS were determined by taking the Fourier transforms of the images. All results are summarized in Table I, where the error in the period measurement is $\sim 10\%$, which includes the calibration uncertainty of the SEM.

As can be seen in Table I, the period of LSFL does not

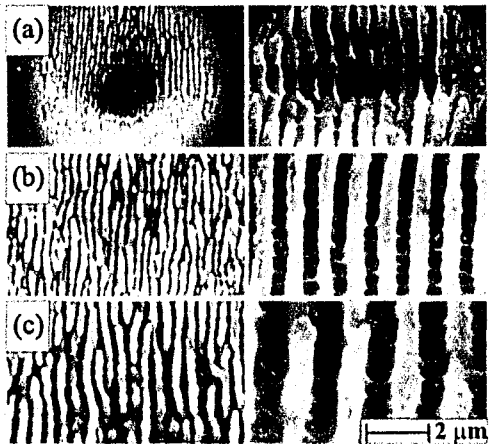


FIG. 2. HSFL (left) and LSFL (right) formed on the surface of (100) GaP after irradiation with (a) 800-nm, (b) 1300-nm and (c) 2100-nm femtosecond pulses.

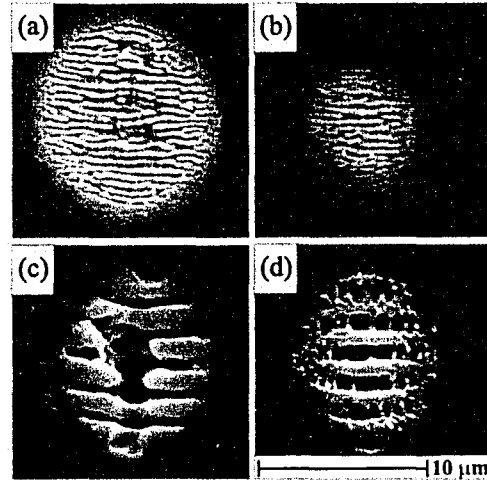


FIG. 3. SEM images of (100) (a) GaP, (b) InP, (c) InAs, and (d) Si surface after irradiation with 20 consecutive pulses at 2100 nm near the respective ablation thresholds.

precisely correspond to the laser wavelength. Departures of the LSFL period from the incident wavelength have been observed previously. For example, Dumitru *et al.*⁸ found ripples with a period of 600–630 nm with 150 fs, 800-nm pulse ablation of ultrahard materials. In addition, 650–750-nm LIPSS periods were observed in 800-nm, femtosecond ablation of Si.¹⁶ The period of our HSFL on III-V semiconductors is 4.2–5.1 times smaller than the laser wavelength. These values are somewhat greater than $\lambda/2n$ (the second harmonics of the incident wavelengths λ) in the unirradiated materials with indices of refraction n). For example, under 2100-nm laser irradiation, the second harmonic wavelength in GaP would be 345 nm, compared to a 410-nm ripple period measured experimentally. Similarly, the period of HSFL on sapphire was ~ 260 nm, close to the second harmonic wavelength of 800-nm light in the solid (226 nm).

TABLE I. Periods of HSFL and LSFL formed on various materials at laser wavelengths of 800, 1300, and 2100 nm. The results are given for similar multiple-pulse irradiation conditions for the respective samples. For a particular material, the values of spatial periods are averages of a number of individual measurements. Symbols: (-) no high-frequency structure observed; (.) no experiment attempted.

Material	Band gap (eV)	Spatial period of LIPSS at given wavelength λ					
		$\lambda = 800$ nm (1.55 eV)		$\lambda = 1300$ nm (0.96 eV)		$\lambda = 2100$ nm (0.59 eV)	
		HSFL	LSFL	HSFL	LSFL	HSFL	LSFL
Si	1.11	-	650	-	1050	-	1600
InAs	0.35	-	700	-	1100	-	1800
InP	1.35	-	680	310	1150	430	1750
GaP	2.26	170	680	300	1050	410	1900
GaAs	1.43	-	-	-	-	470	1650
Ge	0.67	-	-	-	-	-	1800
Sapphire	8.7	260	730	-	-	-	-

We also conducted preliminary experiments on the crystal orientation dependence of HSFL formation on (100) and (110) GaAs for a laser wavelength of 2100 nm. Within the set of parameters investigated, the formation of HSFL was found to be independent of the crystal orientation relative to the polarization of the incident beam, as in the formation of LSFL.² However, the null result should be considered in the context that the present SEM measurements do not characterize the amplitude of the observed features. Additional experiments are planned in order to confirm this conclusion.

The insensitivity of HSFL to crystal orientation of the III-V semiconductor targets suggests that second-harmonic generation in the bulk of undamaged semiconductors does not play a key role, despite the approximate correspondence of some of the HSFL periods and laser second-harmonic wavelengths. However, the compound materials are expected to undergo rapid modification during multiple-pulse irradiation. Thus the near-surface region in the modified materials might facilitate harmonic generation and explain an orientation insensitivity. Initial defects or subsequent laser-induced modification possibly also explain recent observations in the literature on single component diamond-like systems.^{14,15} Ozkan *et al.*¹⁴ reported subwavelength laser writing on diamond crystals and microclusters under multiple-pulse irradiation with a higher number of pulses than utilized here. Yasumaru *et al.*¹⁵ investigated HSFL formation on diamond-like carbon and obtained structures very analogous to those described in the present work. The sample quality (defect density, surface roughness) and specific processing conditions (pulse fluence, number of pulses) might represent key differences between observations on diamond-like systems versus our preliminary investigations on the centrosymmetric crystals Si and Ge. The extent of material segregation or preferential loss of the more volatile element for compounds and the role of material imperfections for single-component samples should be examined in follow-up studies. Furthermore, high-intensity femtosecond light pulses propagating in media are subject to a number of nonlinear effects,¹⁷ complicating arguments based on the initial optical properties of the sample. Detailed analysis should include behavior of the dielectric function of the materials under intense excitation.¹⁸

In summary, we have observed rapid formation of high-spatial-frequency laser-induced periodic surface structures on the surfaces of crystalline compound semiconductors (InP, GaP, and GaAs) and sapphire. HSFL were formed after femtosecond pulse irradiation in the transparency region. A requirement of one-photon transparency has been established. In addition, the present work has elucidated a difference between Si and Ge versus selected III-V semiconductors under the multiple-pulse irradiation range

explored here. Our study complements the observations of Refs. 13–15 by extending the target materials to technologically important semiconductors. The exact mechanism of formation of these patterns is still very much an open question, requiring a detailed theoretical analysis and more experimental studies. Experimental extensions encompassing for example, non-normal incidence, characterization of the ripple amplitudes and stoichiometry, and using a much broader range of laser parameters, should lead to a better understanding of the underlying physics. In addition to purely fundamental interest, the appreciation of high-frequency ripple formation is potentially important for a number of emerging applications in nanotechnology.

Note added in proof. The authors very recently became aware of additional studies on wide band-gap dielectrics which are complementary to our present work on compound semiconductors. The reader is referred to Q. Wu *et al.*, Appl. Phys. Lett. **82**, 1703 (2003), and F. Costache *et al.*, Appl. Surf. Sci. **208–209**, 486 (2003), and references therein.

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¹M. Birnbaum, J. Appl. Phys. **36**, 3688 (1965).

²Z. Guosheng, P. M. Fauchet, and A. E. Siegman, Phys. Rev. B **26**, 5366 (1982).

³J. E. Young, J. E. Sipe, and H. M. van Driel, Phys. Rev. B **30**, 2001 (1984).

⁴J. E. Young, J. E. Sipe, and H. M. van Driel, Opt. Lett. **8**, 431 (1983).

⁵J. S. Preston, H. M. van Driel, and J. E. Sipe, Phys. Rev. B **40**, 3942 (1989).

⁶P. A. Temple and M. J. Soileau, IEEE J. Quantum Electron. **QE-17**, 2067 (1981).

⁷D. Ashkenazi, A. Rosenfeld, H. Varel, M. Wahmer, and E. E. B. Campbell, Appl. Surf. Sci. **120**, 65 (1997).

⁸G. Dumitru, V. Romano, H. P. Weber, M. Sentis, and W. Marine, Appl. Phys. A: Mater. Sci. Process. **74**, 729 (2002).

⁹M. Boile and S. Lazare, Appl. Surf. Sci. **65–66**, 349 (1993).

¹⁰Y. Jee, M. F. Becker, and R. M. Walser, J. Opt. Soc. Am. B **5**, 648 (1988).

¹¹J. J. Yu and Y. F. Lu, Appl. Surf. Sci. **148**, 248 (1999).

¹²D. Bäuerle, *Laser Processing and Chemistry*, 2nd Ed., (Springer, Berlin, 2000).

¹³H. Varel, M. Wahmer, A. Rosenfeld, D. Ashkenazi, and E. E. B. Campbell, Appl. Surf. Sci. **127–129**, 128 (1998).

¹⁴A. M. Ozkan, A. P. Malshe, T. A. Ratkar, W. D. Brown, M. D. Shirk, and P. A. Molian, Appl. Phys. Lett. **75**, 3716 (1999).

¹⁵N. Yasumaru, K. Miyazaki, and J. Kouchi, Appl. Phys. A: Mater. Sci. Process. **76**, 983 (2002) [http://link.springer-ny.com/link/service/journals/00339/first.html].

¹⁶J. Bonse, S. Baudach, J. Krüger, W. Kautek, and M. Lenzner, Appl. Phys. A: Mater. Sci. Process. **74**, 19 (2002).

¹⁷J. C. Diels and W. Rudolph, *Ultrashort Laser Pulse Phenomena: Fundamentals, Techniques and Applications on a Femtosecond Time Scale* (Academic, San Diego, 1996).

¹⁸L. Huang, J. P. Callan, E. N. Glezer, and E. Mazur, Phys. Rev. Lett. **80**, 185 (1998).

The paper outlined the conditions required for formation of HSFL on the surfaces of compound semiconductors. Several speculations as to the physical mechanisms responsible for formation of these structures were also proposed. However, to date, a satisfactory explanation of this phenomenon has not been presented. In contrast to findings presented in this paper, structures resembling HSFL were recently reported on the surface of Si irradiated by a large number of femtosecond pulses ($N > 2 \cdot 10^4$) in ultrahigh vacuum at 800 nm [94,95]. The spatial period of the ripple structures reported in Ref. 94, 95 was ~ 200 nm and the ripples were oriented parallel to the direction of the electric field of the incident pulses. The authors proposed that the patterns originate from surface instabilities, relaxing via self-assembly and ruled out modulated energy input caused by interference, which leads to formation of low spatial frequency LIPSS (LSFL). Preliminary experiments conducted in our laboratory involving irradiation of a Si surface with a large number of pulses, in the transparent region, under rough vacuum, also revealed complicated forms of structural patterning [96]. The patterns observed on Si did not resemble the HSFL reported in Paper 3 or in Ref. 94, 95. One important question which needs to be answered is whether the patterns originate from self-assembly as proposed by the authors in Ref. 94, 95 or if they are driven by the laser field.

The follow up experiments should include the analysis of HSFL formation after irradiation with a laser beam at various angles relative to the surface normal. Formation of LSFL exhibits a definite wavelength dependence and the period of the ripples scales with the angle of incidence of laser beam relative to the sample surface. As shown in this paper the spatial period of HSFL on III-V semiconductors also scales with the wavelength of the incident light. The wavelength dependence of the HSFL spatial period was also reported on TiN and diamond like films irradiated by femtosecond pulses at wavelengths of 800 and 267 nm [64]. Therefore, experiments with non-normal incidence irradiation are a logical follow up. Further experiments should also address the dependence of ripple formation on the polarization of the beam, for example, an extension to circular polarization and rotating linear polarization [97].

The microstructure and chemical composition of HSFL can be investigated by plan-view and cross sectional TEM. Chemical segregation of the compound semiconductors and crystal defects could result from multiple pulse irradiation and influence HSFL formation. At the time of writing of the thesis, several InP samples irradiated with femtosecond pulses centered at 2100 nm were prepared for cross sectional TEM investigation. Three craters, produced with a 1, 5 and 20 consecutive pulses, were selected for detailed cross-sectional TEM investigation. The evolution of the microstructure, chemical composition and potential defects beneath the surface will be investigated.

In addition to fundamental interest, coherent surface structuring has important implications for practical applications. On one hand formation of HSFL and LSFL might limit the precision of laser micromachining and therefore it is important to devise methods for limiting this behavior. On the other hand, in some applications it might be desirable to prepare a corrugated surface, for example, in manufacturing catalysts or in fabrication of diffractive optical elements.

Chapter 5

Micromachining of Grooves in InP

5.1 Introduction

This chapter is based on three previously published papers, which describe the experiments dealing with micromachining and analysis of grooves machined in InP by femtosecond and nanosecond laser pulses. The work reported addresses issues more closely related to potential applications of femtosecond laser pulses in scribing and dicing of InP or other semiconductors. These issues include the following: analysis of the ablation rates, the geometry and the morphology of the grooves, and the effects of the machining process on the surrounding material. The reprints of the contributions are preceded by short introductions. Additional comments on each paper with possibilities for follow up investigations are included at the end of each section.

5.2 Paper 4 –Femtosecond micromachining of grooves in InP

This paper deals with the analysis of the ablation rates, and the geometry and morphology of grooves micromachined in InP by femtosecond laser pulses. Although the concept behind these experiments is straightforward, at the time of the investigations there were no analogous reports of systematic characterization of femtosecond laser micromachining of InP or other semiconductors. The work presented in this publication is a natural extension of single and multiple pulse experiments presented in Chapter 4, and by other groups [53,55,56], involving irradiation of stationary samples. In this paper, the effects of pulse energy, feed rate, number of consecutive passes over the same area, and the polarization of the beam relative to the cutting direction were investigated. The results were discussed in terms of results obtained from single and multiple pulse irradiation and in the broader context of femtosecond laser machining of other materials

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Femtosecond laser micromachining of grooves in indium phosphide

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ABSTRACT Femtosecond laser micromachining of indium phosphide is investigated using 150 fs light pulses at a center wavelength of 800 nm. The ablation rate for micromachining of grooves is investigated as a function of pulse energy, feed rate, number of passes over the same groove, and the light polarization relative to the cutting direction. A logarithmic dependence of the groove depth on the laser fluence is observed with two regimes characterized by different ablation rates and different thresholds. The groove depth is found to be inversely proportional to the feed rate or equivalently linearly proportional to number of pulses delivered per unit area. With multiple passes over the same groove the depth increases linearly up to about 20 consecutive passes. Above 20 passes the ablation rate decreases until a depth limit is approached. The best results in terms of groove geometry and depth limit are obtained with the polarization of the beam perpendicular to the cutting direction.

PACS 42.62.Cf; 79.20.Ds; 81.20.Wk

1 Introduction

Laser-based processing of semiconductors has long been an area of intense investigation due to its technological importance. Much early work was aimed at laser assisted annealing of ion implanted Si and the experiments were performed with nanosecond and continuous wave lasers [1]. The development of ultrafast laser sources has stimulated interest in the application of sub-nanosecond lasers for modification of semiconductors [2]. Initially the research was mainly aimed at the study of ultrafast phase transitions and lattice dynamics under intense excitation [3, 4]. With rapid technological advances in ultrafast laser technology, the tremendous potential of femtosecond laser pulses as a material processing tool has been demonstrated by many groups (see e.g., [5–10]). Now ultrafast laser technology has entered the industrial market and there is an increasing need for systematic analysis and characterization of various materials machined by femtosecond lasers. In practical applications

such as drilling, cutting or scribing, one must find a set of parameters which provide the desired results under particular processing constraints. The laser parameters typically include pulse energy, repetition rate, feed rate, spot size, pulse duration and laser wavelength. Typical constraints include material properties, desired feature quality, feature size, and throughput. In this work we present the study of micromachining of grooves in InP by 150 fs, 800 nm laser pulses with an emphasis on the characterization of ablation rates, geometry and morphology of the machined features. InP is a widely used III-V compound semiconductor especially in optoelectronic and high-speed electronic applications. The electronic, optical and physical properties of InP have been studied extensively [11]. The work presented here is an extension of experiments involving single and multiple pulse ablation of InP recently reported by a few groups [12, 13].

2 Experimental Setup

The machining experiments on InP were performed with a commercial 1 kHz amplified Ti:sapphire laser system (Spectra Physics Spitfire). The laser produced ≈ 150 fs pulses centered around a wavelength of 800 nm. The laser was focused on the sample by a $5\times$ microscope objective (Newport M-5 $\times$) to a spot size of $\omega_0 \approx 5 \mu\text{m}$ (beam radius measured at $1/e^2$). The far-field intensity distribution after the objective was measured with a CCD beam profiler (Ophir BeamStar) and to a good approximation followed a Gaussian distribution. The pulse energy on the sample was adjusted with a combination of a half-wave plate and a thin film polarizer followed by a set of thin metallic neutral density filters. In most experiments the pulse energy was less than 2 μJ . The pulse energy was measured with a calibrated semiconductor power meter (Ophir PD300-3W). An uncertainty in the fluence measurement of approximately $\pm 20\%$ is attributed to the laser energy fluctuations and uncertainty in the spot size measurements. InP wafers (Acrotec) were placed inside a small vacuum chamber ($p \lesssim 0.1$ mbar) mounted on a precision, computer-controlled xy translation stage with step resolution of less than 1 μm and a maximum linear speed of 1000 $\mu\text{m/s}$. Sets of parallel grooves were cut in samples of (100) *n*-InP under various conditions, namely variable pulse energy, feed rate, number of consecutive passes over the same groove and polarization relative to the cutting direction. The machining

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process was monitored on-line with a confocal CCD camera. Processed samples were cleaved perpendicular to the grooves and the cross-section of the micromachined features was analyzed with a scanning electron microscope (Philips SEM 515). The instrumental error in the depth measurement was approximately $\pm 5\%$.

3 Results

Single pulse ablation measurements were performed on every sample to determine the spot size on the surface and the ablation threshold [14]. The results of these single pulse measurements are useful in the analysis of groove cutting results. Single femtosecond pulses, with fluences above the ablation threshold, produce craters on the surface with a characteristic rim, which marks the boundary of the ablated area [12, 15]. In the analysis, the crater diameter (D), measured to the outside of the rim, was measured as a function of pulse energy (E_0), and the ablation threshold pulse energy (E_{th}) as well as the spot size (ω_0) were determined by fitting the data according to [12, 14]

$$D^2 = 2\omega_0^2 \ln \left(\frac{E_0}{E_{th}} \right). \quad (1)$$

Under tight focusing conditions the rim thickness is significant compared to the total dimensions of the crater. Experimentally it is most convenient to measure the diameter to the outside of the rim. Following other morphological features, such as the inside crater diameter will give somewhat different threshold energy. All crater measurements presented in this work were measured to the outside rim of the crater. With the obtained fit parameters the peak fluence (ϕ_0) was calculated from the formula

$$\phi_0 = \frac{2 \times E_0}{\pi \omega_0^2}. \quad (2)$$

The typical experimental data and the fit to (1) are shown in Fig. 1. The uncertainties in the obtained fit parameters reflect only the uncertainty for the fitting routine. In this particular data set the least squares fit yields a spot size of $5.1 \pm 0.3 \mu\text{m}$. In a larger set of experiments performed over a period of months, the spot size varied from 5 to $6 \mu\text{m}$. The variation is mainly attributed to the inherent uncertainty in sample positioning with respect to the objective. From the data we obtain the single pulse ablation threshold fluence $\phi_{th}(1) = 166 \pm 8 \text{ mJ/cm}^2$. The average value of the ablation threshold measured over a large set of experiments yields the value of 170 mJ/cm^2 , which is slightly higher than our previously reported value [16].

In addition to the single pulse ablation experiments, we have measured the ablation threshold after exposure to multiple pulses. The decrease of the ablation threshold with an increasing number of pulses is well known and has been studied in many materials including metals [17, 18], dielectrics [19], ceramics [20] and semiconductors [12, 21]. The decrease of the ablation threshold is usually explained in terms of incubation effects [19]. The ablation threshold $\phi_{th}(N)$ after irradiation with N pulses, is related to the single pulse ablation threshold $\phi_{th}(1)$ by the relation [12, 17, 21]

$$\phi_{th}(N) = \phi_{th}(1) \times N^{\xi-1}, \quad (3)$$

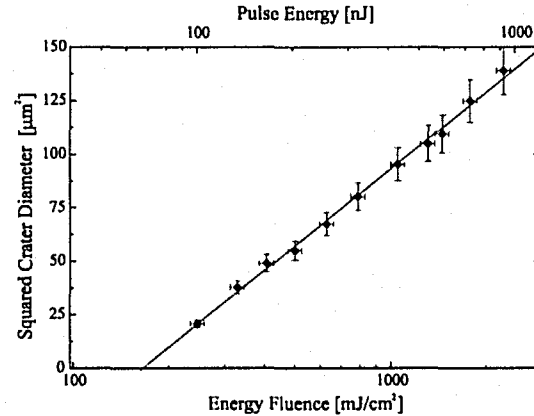


FIGURE 1 Squared diameter D^2 of single pulse ablation craters as a function of the peak laser fluence (pulse energy) and a least squares fit to (1) (solid line). Note that the error bars on the x-axis represent the uncertainty in pulse energy measurement

where ξ characterizes the degree of incubation. The value of $\xi = 1$ implies an absence of incubation with the ablation threshold being independent of the number of pulses. The total accumulated fluence at the ablation threshold after 1, 5, 10, 20, 50 and 100 consecutive laser pulses is shown in Fig. 2 along with the fit to (3). The fit yields $\xi = 0.74 \pm 0.09$. The uncertainty in the diameter measurements of craters produced by multiple pulse irradiation is greater than in single pulse experiments since the ablation rim marking the perimeter of the crater is obscured by surface debris and periodic surface structuring. This leads to higher uncertainties in the threshold measurements and therefore a relatively large uncertainty in the measured value of the incubation coefficient ξ .

In the process of groove cutting, the sample is exposed to multiple pulses while being continuously translated at feed rate v . It is convenient to express the feed rate in terms of an effective number of pulses delivered in order to compare

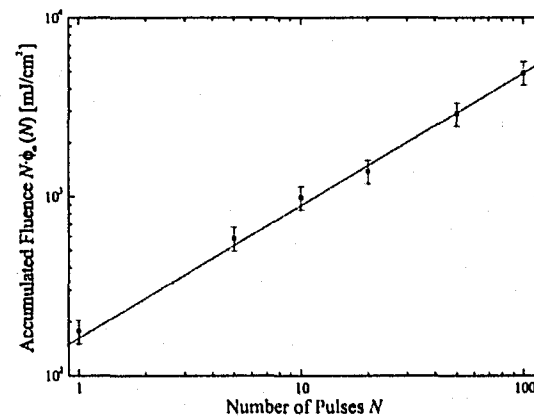


FIGURE 2 Accumulated fluence at the ablation threshold $N \times \phi_{th}(N)$ as a function of the number of pulses N delivered and a least squares fit to (3) (solid line)

the results to stationary processing. The approximate relation derived for the effective number of pulses incident along the center of the groove (N_{eff}) is given by

$$N_{\text{eff}} = \sqrt{\frac{\pi}{2}} \frac{\omega_0 f}{v} \quad (4)$$

where $f = 1$ kHz is the repetition rate of the laser. The expression was derived by calculating the accumulated fluence of a series of pulses with a Gaussian intensity profile, peak fluence of ϕ_0 and separated by v/f , the distance travelled between pulses. It is important to point out that this is an approximate relation and is not expected to be completely equivalent to stationary processing with N pulses. Nevertheless it is instructive in a first analysis of the groove cutting results. In the subsequent discussion, all the references to the effective number of pulses delivered are based on conversion of the feed rate v to the effective number of pulses N_{eff} via (4).

In the first set of groove cutting experiments, the groove depth was measured as a function of pulse energy (fluence) in the range of $E_0 = 20$ – 2000 nJ/pulse ($\phi_0 \approx 49$ – 4900 mJ/cm²), at feed rates of 100, 250 and 500 $\mu\text{m/s}$. In all experiments the polarization of the beam was linear and perpendicular to the scan direction, unless explicitly stated otherwise. The results are shown in Fig. 3 and selected SEM images of grooves are illustrated in Fig. 4. The groove depth (h) exhibits a logarithmic dependence on the pulse energy (fluence) and can be fit to an equation of the form

$$h(\phi_0) = h_0 \times \ln \left(\frac{\phi_0}{\phi_{\text{th}}} \right) \quad (5)$$

where h_0 and ϕ_{th} are the fit parameters. The fit parameter h_0 represents the groove depth at fluence $e \times \phi_{\text{th}}$ ($e = 2.718$...) for a given feed rate. The average ablation depth per pulse (l), at fluence $e \times \phi_{\text{th}}$, can be obtained by dividing the groove depth h_0 by the effective number of pulses calculated from (4) and yields $l = h_0/N_{\text{eff}}$. The fit parameter ϕ_{th} represents

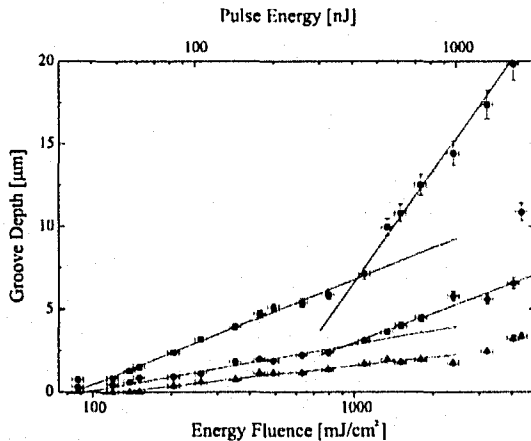


FIGURE 3 Groove depth as a function of the laser fluence (pulse energy) for feed rates of 100 (■), 250 (●) and 500 (▲) $\mu\text{m/s}$. The solid lines are the fit according to (5). Note that the error bars on the x-axis represent the uncertainty in pulse energy measurement

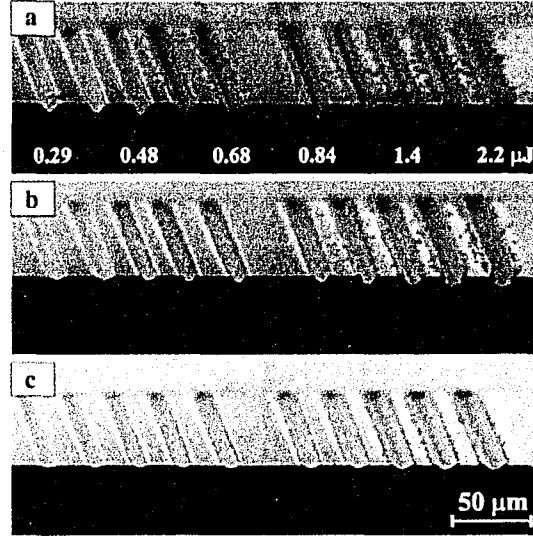


FIGURE 4 SEM images of grooves machined at feed rates of a 100, b 250 and c 500 $\mu\text{m/s}$. Pulse energies [μJ] for selected grooves are shown in Fig. 4a. Note that each image is a montage of two separate SEM images

the generalized ablation threshold for grooves cut with specified parameters. Two distinct regimes, with different slopes and different thresholds are clearly seen in Fig. 3, especially at a feed rate of 100 $\mu\text{m/s}$. At higher feed rates, above 500 $\mu\text{m/s}$, the second regime is evident if the pulse energy is extended beyond 2 μJ ; however, with the current data set, a satisfactory fit in the second regime was not obtained at this feed rate. The two regimes are sometimes termed gentle and strong ablation and this terminology will be adopted in the current paper. Subscripts g and s will be used to distinguish quantities corresponding to the two regimes where applicable. The obtained fit parameters for the three different feed rates in the gentle and strong ablation regimes are summarized in Table 1.

In the next set of experiments, the pulse energy (fluence) was held constant at $E_0 = 1060, 370$ and 120 nJ ($\phi_0 \approx 1900, 650, 210$ mJ/cm²) and the dependence of the groove depth on the feed rate was investigated in the range of $v = 50$ – 1000 $\mu\text{m/s}$ ($N_{\text{eff}} = 150$ – 8). In this set of experiments, the spot size on the sample surface was measured to be 6.0 ± 0.3 μm . The groove depth was found to be inversely proportional to the feed rate, scaling as v^{-1} . Equivalently, plotting the same data as a function of the effective number of pulses

Feed Rate [$\mu\text{m/s}$]	Gentle Ablation					Strong Ablation				
	N_{eff}	h_g [μm]	l_g [nm]	E_{th} [nJ]	ϕ_{th} [mJ/cm ²]	h_s [μm]	l_s [nm]	E_{th} [nJ]	ϕ_{th} [mJ/cm ²]	
100	64	2.8	44	35	86	9.2	144	190	460	
250	26	1.2	46	38	93	2.6	100	130	320	
500	13	0.8	62	48	120	–	–	–	–	

TABLE 1 Summary of the fit parameters obtained after fitting the data in Fig. 3 to (5)

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calculated from (4) yields a linear dependence of the groove depth on the effective number of pulses. The groove depth as a function of feed rate and effective number of pulses was first fitted to the simple empirical expressions:

$$\begin{aligned} \text{(a)} \quad h(v) &= \frac{A}{v} \\ \text{(b)} \quad h(N_{\text{eff}}) &= B \times N_{\text{eff}} \end{aligned} \quad (6)$$

where A and B are the empirical fit parameters which are summarized in Table 2. The parameter B represents the average ablation rate (ablation depth per pulse) at specified pulse energy (fluence). For comparison [12], data was also fitted to (5) with ϕ_{th} approximated by $\phi_{\text{th}}(N_{\text{eff}})$ in (3) and h_0 replaced with $l \times N_{\text{eff}}$. In the fit only l was used as the free parameter, and $\phi_{\text{th}}(1)$ and ξ were fixed at 170 mJ/cm^2 and 0.74 , respectively obtained from single and multiple pulse measurements. The experimental data and the linear fit to (6b) (solid line) and the nonlinear fit to (5) with the above substitutions (dashed line) are shown in Fig. 5 and the SEM images of some of the corresponding grooves are shown in Fig. 6. The values of l obtained for pulse energies (fluences) of $E_0 = 1060, 370$ and 120 nJ ($\phi_0 \approx 1900, 650, 210 \text{ mJ/cm}^2$) are $l \approx 90, 50$ and 50 nm , respectively.

In cases where the desired groove depth or the groove geometry cannot be attained with a single pass, several passes over the same region are required. In the third set of experiments, the dependence of the groove depth on the number of consecutive passes over the same groove was investigated with pulse energy (fluence) $E_0 = 1060, 370$ and 120 nJ/pulse ($\phi_0 \approx 1900, 650, 210 \text{ mJ/cm}^2$) and feed rate $v = 500 \text{ } \mu\text{m/s}$. The results are shown in Fig. 7 and the corresponding SEM image of the grooves are shown in Fig. 8. The depth of the grooves increases linearly with an increasing number of passes over the same groove up to about 20 consecutive passes as seen in Fig. 7a. The removal rates for pulse energies of $E_0 = 1060, 370$ and 120 nJ/pulse are $2.4, 1.2$ and $0.6 \text{ } \mu\text{m/pass}$ ($B = 160, 80$ and 40 nm/pulse) respectively. Beyond approximately 20 passes, the feature depths increase at a slower rate until an asymptotic depth limit is reached as seen in Fig. 7b. To a good approximation, the depth limit was reached after 100 consecutive passes at all pulse energies investigated. The depth limit exhibits a logarithmic dependence on the pulse energy (fluence) and can be fitted very well to (5). Figure 9 shows the plot of the groove depth cut at feed rate of $500 \text{ } \mu\text{m/s}$ and 100 passes/groove, as a function of pulse energy (fluence) and the fit to (5). The two ablation regimes are clearly seen, with the point of inflection around 1 J/cm^2 and the fit parameters $h_g = 17 \pm 1 \text{ } \mu\text{m}$ and $\phi_{\text{th}} = 73 \pm 5 \text{ mJ/cm}^2$ in the gentle regime and $h_s = 42 \pm 2 \text{ } \mu\text{m}$ and $\phi_{\text{th}} = 250 \pm 30 \text{ mJ/cm}^2$ in the strong ablation regime.

E_0 [nJ]	ϕ_0 [mJ/cm ²]	A [$\mu\text{m}^2/\text{s}$]	B [nm]
1060	1900	1400	195
370	650	620	80
120	210	320	50

TABLE 2 Summary of fit parameters obtained after fitting the data in Fig. 5a and b to (6a) and (6b) respectively

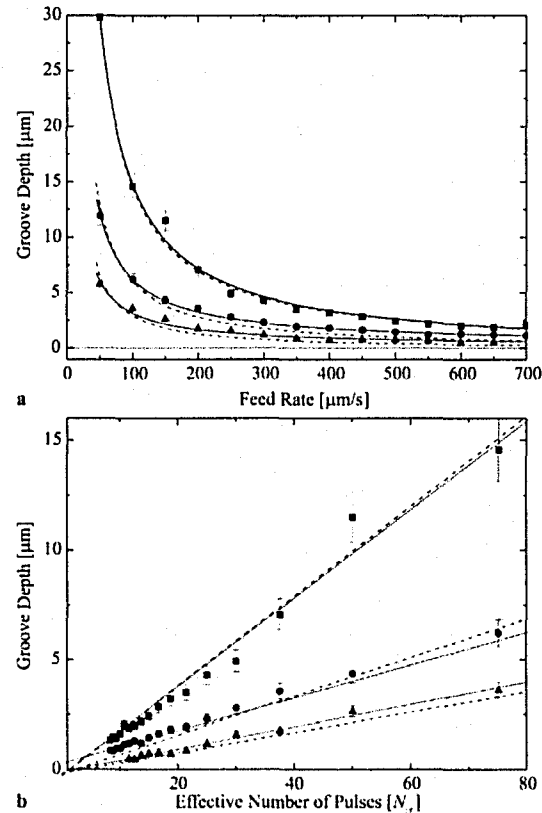


FIGURE 5 Groove depth as a function of feed rate a and the effective number of pulses b calculated with (4) for pulse energies $E_0 = 1060$ (■), 370 (●) and 120 (▲) nJ/pulse. The solid line represents a fit according to (6a) and (6b) and dashed line fit to (5) with substitutions specified in the text

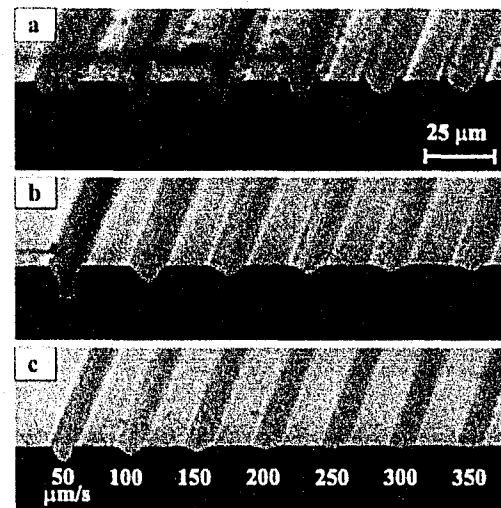


FIGURE 6 SEM images of grooves cut at feed rates ranging from 50 to $350 \text{ } \mu\text{m/s}$ and pulse energies of a 1060 , b 370 , and c 120 nJ/pulse

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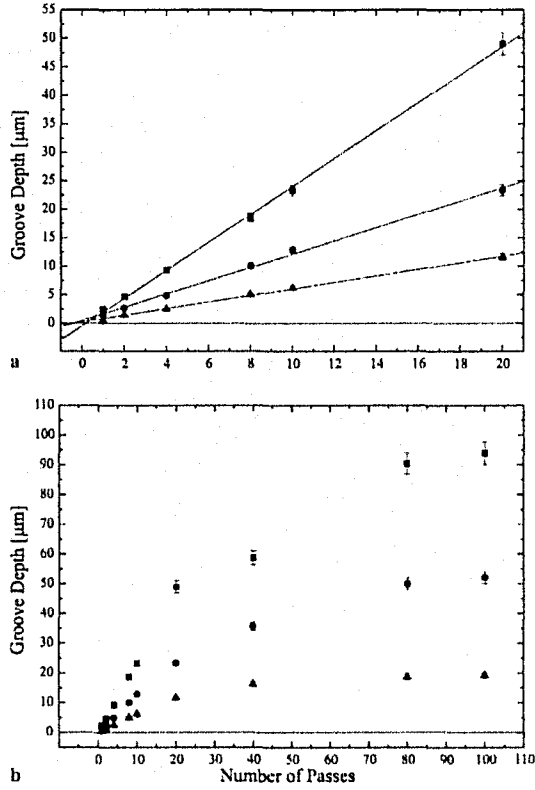


FIGURE 7 Groove depth as a function of the number of consecutive passes over the same groove. a shows the linear portion up to 20 passes/groove, while b illustrates the full data set up to 100 passes/groove for pulse energies $E_0 = 1060$ (■), 370 (●) and 120 (▲) nJ/pulse

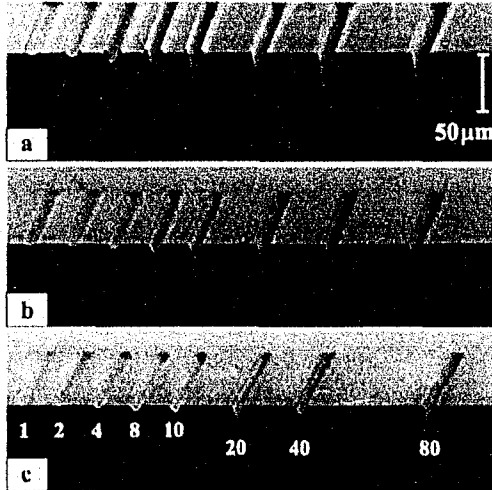


FIGURE 8 SEM images of grooves cut with a 1060, b 370 and c 120 nJ/pulse, cutting speed of 500 μm/s and number of consecutive passes ranging from 1 to 80. The number of passes for each groove is indicated on c. Note that each image is a montage of three separate SEM images

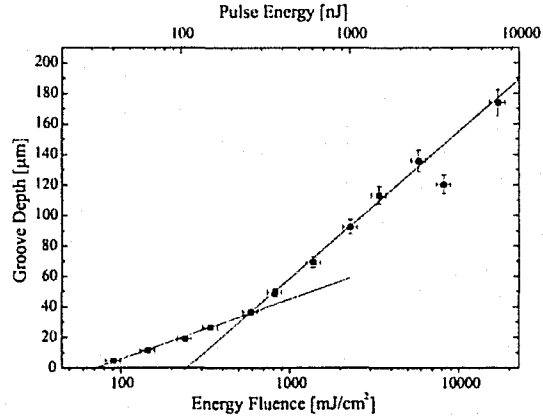


FIGURE 9 Dependence of the groove depth cut at feed rate of 500 μm/s and 100 consecutive passes/groove ($N_{eff} = 1300$ pulses) as a function of peak pulse fluence (pulse energy). The solid line represents fit to (5). Note that the error bars on the x-axis represent the uncertainty in pulse energy measurement, and that the laser spot size for this case was 5.3 μm

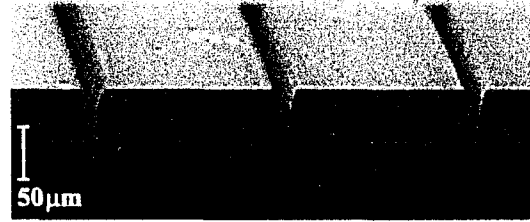


FIGURE 10 Three trenches cut with 370 nJ/pulse at 500 μm/s and 100 passes/groove with polarization varied from (left) parallel to the cutting direction, (middle) perpendicular, and (right) circular polarization

The polarization of the beam relative to the cutting direction is an important factor, especially in multiple pass cutting. Figure 10 shows an SEM image of three trenches cut in a separate experiment with $E_0 = 370$ nJ/pulse, 100 passes per groove, cut at 500 μm/s with (left) linear polarization parallel, and (middle) perpendicular to the cutting direction; and (right) with circular polarization. Under our experimental conditions the best results, both in terms of the depth limit as well as the groove geometry, were obtained with a polarization perpendicular to the cutting direction.

4 Discussion

We have presented the results of femtosecond micromachining of InP with an emphasis on measurement of the dependence of the groove depth or ablation rate of InP on the pulse energy (fluence), feed rate, and number of consecutive passes over the same groove. The data for the groove depth versus the laser fluence can be fit by a logarithmic dependence - with two regimes characterized by different ablation rates I and different ablation thresholds ϕ_{th} . In the gentle ablation regime, below a fluence of 1 J/cm² and with a feed rate of 100 μm/s ($N_{eff} = 64$), average ablation depth at $e \times \phi_{th}$, $I_g \approx 44$ nm obtained from our measurements is in

good agreement with values published by other authors. In similar experiments involving micro-hole drilling in InP, Bonse et al. [12] obtained a value of $l_s \approx 30$ nm by measuring the depth of ablation craters produced by $N = 100$ consecutive pulses as a function of pulse energy in the fluence range $\phi_0 = 0.5\text{--}5 \text{ J/cm}^2$. The difference in the measured ablation rate could be accounted for by somewhat different experimental conditions. The most significant difference is the fact that in our experiment the sample is continuously translated while all experiments performed by Bonse et al. involve irradiation of stationary samples. Also in our experiment, we utilize tight focusing with spot size typically below $6 \mu\text{m}$ and all of our experiments were performed in vacuum. Experiments conducted by Bonse et al. were performed in air with $f = 60$ mm lens ($\omega_0 \approx 23 \mu\text{m}$) used as a focusing element. Nevertheless, within the experimental uncertainty the overall agreement is good.

Equation (5), used to fit our data, has the same form as the well known expression for single pulse ablation depth (see [22]), $d(\phi_0) = \alpha^{-1} \ln(\phi_0/\phi_{th})$, where α^{-1} is the optical penetration depth. Hence, for fluences of a few times the threshold value, the single pulse ablation depth l , would be comparable to the optical penetration depth α^{-1} . In ablation of metals, the values of l obtained by measuring the ablation depth per pulse is typically close to the values of α^{-1} . For example, Nolte et al. [23] measured $l = 10$ nm in ablation of copper targets (150 fs, 800 nm), compared to the optical penetration coefficient for copper of $\alpha^{-1} = 13$ nm. Preuss et al. [24] performed similar experiments on nickel, copper, molybdenum, indium, tungsten and gold with 500 fs, 248 nm pulses. They obtained good overall agreement between the ablation depth and the optical penetration coefficient for nickel, copper and molybdenum, while values for indium, tungsten and gold differed by factor of 6, 4, and 3, respectively. The value of α^{-1} for InP measured by spectroscopic techniques at a wavelength of 800 nm is $\alpha^{-1} \approx 305$ nm [25] and is an order of magnitude higher than values of l reported in the current study and by Bonse et al. [12]. Similar results were previously reported in ablation of Si with 300 fs pulses, at a wavelength of 612 nm. Kautek and Krüger [26] reported single pulse ablation depth of $l \sim 100$ nm in the gentle ablation regime for Si compared to the optical penetration coefficient for Si of $\alpha^{-1} \approx 2.5 \mu\text{m}$ at wavelength of 612 nm. However, the techniques of optical penetration coefficient measurement involve very low intensity sources. In femtosecond ablation, nonlinear processes become important. Recent studies on GaAs reveal substantial changes of the dielectric function under intense excitation below damage threshold [27]. Therefore, in the case of semiconductors, the nonlinear absorption must be taken into account in order to make a comparison between l and α^{-1} [21, 26]. Furthermore, in multiple pulse irradiation and groove cutting experiments the semiconductor surface will undergo chemical and structural changes [16, 28] after the first few pulses, which makes a comparison based on the initial sample properties less accurate.

The existence of two ablation regimes was reported in femtosecond ablation of other materials, such as metals [23, 29, 30], ceramics [31, 32] and dielectrics [33]. In our measurements the value of l in the strong ablation regime is higher than in the gentle ablation regime by a factor of 2–3. The

measured values of both l and ϕ_{th} in the strong ablation regime for InP are similar to values reported for ablation of metals. For example, in experiments dealing with femtosecond ablation of copper [23], Nolte et al. reported $l_s = 80$ nm and $\phi_{th} = 460 \text{ mJ/cm}^2$ (150 fs, 800 nm). Furusawa et al. [29], measured $l_s = 103$ nm and $\phi_{th} = 397 \text{ mJ/cm}^2$ in femtosecond ablation of silver samples (120 fs, 780 nm) and Venkatakrishnan et al. [30] measured $l_s = 71$ nm and $\phi_{th} = 270 \text{ mJ/cm}^2$ in femtosecond groove cutting in gold films (150 fs, 400 nm).

In experiments involving the measurement of the groove depth dependence on the feed rate (effective number of pulses), we observe an inverse dependence on the feed rate or equivalently linear dependence on the effective number of pulses delivered. Our results are once again consistent with micro-hole drilling measurements of Bonse et al. [12]. With the fluence kept constant at $\phi_0 \approx 650 \text{ mJ/cm}^2$ and groove depth measured as a function of the feed rate in the range $v = 50\text{--}1000 \mu\text{m/s}$ ($N_{eff} = 150\text{--}8$) we measure the ablation rate of $B = 80 \pm 5 \text{ nm/pulse}$ by using (6b) to fit the data. In micro-hole drilling experiments, with laser fluence kept constant at $\phi_0 = 580 \text{ mJ/cm}^2$ and crater depth measured as a function of number of pulses ($N = 8\text{--}500$), Bonse et al. measured $B = 86 \text{ nm/pulse}$.

The results for the groove depth dependence on the feed rate (effective number of pulses) were also fitted to (5) with substitutions specified earlier; however, a good fit was only obtained for a pulse energy of $E_0 = 1060 \text{ nJ}$. In this case, it is important to point out that fitting data relies on the knowledge of the single pulse ablation threshold ϕ_{th} (1), the incubation coefficient (ξ) and the spot size (ω_0). Each of these quantities carries substantial uncertainties and the combined uncertainty in all of these quantities can change the value of the fit parameter l by as much as $\pm 40\%$. Nevertheless, the value obtained from the fit, $l \approx 50 \text{ nm}$ for $E_0 = 370 \text{ nJ}$, is consistent with our previous measurements and with a value obtained by Bonse et al. [12], $l \approx 33 \text{ nm}$, obtained under similar conditions.

A linear dependence of the ablation depth on the number of pulses was observed in femtosecond ablation of other materials. For example, in experiments on irradiation of various glasses, Lenzner et al. [34] found a linear dependence of the ablation depth on the number of pulses for pulse duration varying from 5 to 500 fs at laser fluence of $6.2 \pm 0.7 \text{ J/cm}^2$. Single pulse ablation rates varied from 250 nm/pulse at 500 fs to 125 nm/pulse at 5 fs. Ameer-Beg found an inverse dependence of the groove depth on the feed rate, scaling approximately as v^{-1} , in experiments dealing with ablation of fused silica, Pyrex and silicon [35]. Dumitru et al. [9] presented results for femtosecond ablation of ultra-hard materials, and reported ablation rates of 175–185, 125, 130 and 90 nm/pulse for femtosecond ablation of tungsten carbide, titanium carbide, titanium nitride and diamond respectively at a fluence of $\sim 6.2 \text{ J/cm}^2$. The ablation rates in the high fluence range are comparable to ablation of InP in the strong ablation regime. With the fluence kept constant at $\sim 1.9 \text{ J/cm}^2$, we measured an ablation rate of 195 nm/pulse.

In machining deep grooves, the ablation rate decreases with an increasing number of passes (pulses) and departs from the linear dependence. The mechanism of this effect can be considered. As the trench depth increases, it starts to act as

a hollow waveguide. The initial pulse must first travel to the bottom of the groove, where the majority of the ablation takes place. During laser pulse propagation through the groove the pulse energy decreases due to scattering and absorption. Consequently, the energy available for ablation at the bottom of the groove is diminished, resulting in a reduced ablation rate. At some final depth, the propagation losses are sufficiently high to bring the pulse energy below the ablation threshold. Furthermore, with increasing depth material ablated at the bottom has a greater probability of redepositing on the walls, leading to an unavoidable taper. Similar behavior has been observed in femtosecond processing of different glasses [36].

All of the results in this paper were obtained under rough vacuum conditions. However, in practical applications, it is desirable to avoid potentially expensive and cumbersome vacuum equipment. The differences between machining in air and in vacuum are expected to be similar to the results obtained by Wynne and Stuart [37] who investigated the rate dependence of short-pulse laser ablation of metals in air and in vacuum. They observed only a minor difference between ablation rates in air and in vacuum for shallow features with a $\sim 1:1$ aspect ratio. With an increasing aspect ratio $\sim 10:1$, the difference became significant with ablation rates in air being 2–10 times lower than in vacuum depending on the material. We might expect analogous effects in micromachining of semiconductors and such experiments could be a subject of separate investigation.

The ablation rate (depth/pulse) increases with increasing pulse energy, especially after the onset of strong ablation. However, this is also accompanied by an increased amount of debris and redeposition of the ablated material in the vicinity of the cut. This is well illustrated in the SEM images in Figs. 4 and 6. In the case of low feed rates and high pulse energies, the removal of ablated material from inside the groove is problematic and in many cases the expelled material solidifies inside the groove, leading essentially to a sealed trench (Fig. 6a). The debris accumulated at the surface is less problematic and can be easily removed with methanol and lens tissue or an ultrasonic bath. Surface debris might be problematic in micromachining tightly spaced features as debris ejected from the adjacent grooves might affect the cutting of subsequent grooves. Within the range of our experimental parameters, the best results, in terms of groove morphology, geometry and minimum material redeposition were obtained with low pulse energies $\approx 3\phi_{th}$, high scan rates, and with a large number of consecutive passes. Our current results suggest that high repetition rate systems ~ 10 – 100 kHz employing high-speed scanning mirrors or acousto-optic deflection [38] would be the most suitable for high speed precision machining, allowing high throughput and the best feature quality.

In practical applications, the polarization dependence of the cutting direction must be addressed. The dependence of the ablation efficiency on the polarization direction is a well known phenomenon in conventional laser cutting applications where the cutting rate can vary by as much as a factor of two [39]. In the context of our experiments, we need to consider two cases, single and multiple pass cutting. In single pass cutting, the laser is incident at normal incidence relative to the cutting surface but at a glancing angle relative to the erosion front. At glancing incidence, there is a distinct difference

between s and p polarization: s -polarization will suffer high reflectivity losses, while p -polarization will be preferentially absorbed giving rise to different ablation rates. For this reason, many commercial laser cutting stations are equipped with a $\lambda/4$ plate [39], to convert the beam to circular polarization and to ensure that the ablation rate is uniform in all directions. The second situation encountered in our experiments is the multiple pass cutting. Here, the light incident on the surface must first travel to the bottom of the groove where the majority of the ablation takes place as discussed above. During propagation through the groove, the light will experience reflections and scattering at the sidewalls. The intensity of the reflected light will depend on the polarization of the light relative to the side walls. One might expect that s -polarization (relative to the side walls) might yield better results due to the higher reflectivity and, therefore, better guiding; however, that is not the case (as seen in Fig. 10). The trenches become asymmetric with a characteristic bend near the bottom. Bärsch et al. [40] observed similar effects in ablation and cutting of thin silicon wafers. The authors report substantial improvements in the geometry of the exit hole when the polarization of the beam is perpendicular to the scan direction.

The effects of polarization in femtosecond laser micro-drilling of steel were reported by Nolte et al. [41]. The main thrust of their experiments was the investigation of the geometry of the high aspect holes, and particularly the dependence of the geometry of the exit holes on the light polarization. It was discovered that drilling with linearly polarized light leads to non-circular exit holes. In order to overcome this problem, the group employed 'polarization trepanning' – where a $\lambda/2$ plate is rotated during drilling – in essence scrambling polarization. This technique yielded superior results compared with linear and even circular polarizations. The effects of polarization on ultrashort pulse ablation of thin metals were recently reported by Venkatakrishnan et al. [42]. The authors reached analogous conclusions, in so much that the polarization of the beam plays an important role in determining the ablation depth, edge quality, kerf width and the cutting rate of machined features.

Bonse et al. [43] have performed a number of experiments dealing with the polarization dependence of femtosecond ablation of TiN. In experiments with 130–150 fs, 800 nm pulses, the authors observed an increase in ablation rate for circularly polarized beams compared to linear polarization. After 100 pulses at $\phi_0 = 0.43 \text{ J/cm}^2$, the volume of material removed with circular and linearly polarized beams was ~ 340 and $110 \mu\text{m}^3$, respectively. Observed ablation rates for multiple pulse irradiation were 12.6 nm/pulse and 9.1 nm/pulse for irradiation with circular and linearly polarized pulses. The authors also quantified average roughness of the ablated craters and found 2–3 times reduction of the average roughness in craters ablated with circularly polarized light.

In addition to laser ablation, work on laser-assisted dry etching of InP involving use of excimer lasers in the presence of a halogen atmosphere has been reported [44, 45]. Prasad et al. [44] used a 10% gas mixture of chlorine diluted in helium in an investigation of etch rates with 308 nm light. Laser-assisted (308 nm) dry etching of InP in low-pressure chlorine atmospheres at fluences lower than the ablation threshold has been studied by Wrobel et al. [45]. Matz et al. have

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demonstrated practical application of this technique in dry etching of integrated InP micro-lenses using a 248 nm excimer laser [46]. These chemically-assisted dry etch schemes using nanosecond UV lasers offer an interesting, complementary approach to femtosecond laser micromodification. Bäuerle [22] provides a comprehensive overview of theory and experiments of laser assisted etching. Femtosecond assisted etching in Cl_2 and SF_6 atmosphere [47, 48] has been attempted on Si surfaces, yielding the formation of high aspect ratio spikes. Such features on Si have attracted attention as potential light absorbers in solar cells and photodetectors.

Currently semiconductor processing largely involves well-established photolithography technology, and it is unlikely that direct laser patterning would replace it in the near future. However, the laser tools can play an important role in dicing, prototyping, trimming and device repair. Bärsch et al. [40] have recently presented results of cutting silicon wafers with femtosecond laser pulses. Dupont et al. [49] have demonstrated the use of femtosecond laser ablation for in-situ repair of optoelectronic devices. Such techniques might be very valuable especially in manufacturing of large area CCD or LED arrays where removing a few local defects can significantly increase the device yield.

Interest in femtosecond laser ablation and machining encompasses a broad range of materials, including rather specialized compounds and applications. With the growing importance of gallium nitride (GaN), for example, direct laser patterning might also be an important application due to lack of suitable chemical etch solutions. Femtosecond laser micromachining of GaN was discussed by Kim et al. [50]. In machining grooves in GaN samples, the authors reported the ablation rates between 2–3 $\mu\text{m}/\text{pass}$ at feed rates ranging from 300 to 3000 $\mu\text{m}/\text{s}$ and laser fluence of 1 J/cm². Ultrafast laser processing is also very promising for other materials related to the semiconductor industry. Femtosecond machining of AlN [31] and diamond films [8], which are used as heat sinks, and other hard materials [9] has been shown to yield superior results to machining with conventional lasers.

5 Summary

We have presented results of femtosecond micro-machining of InP with 150 fs laser pulses centred at 800 nm, and utilizing a repetition rate of 1 kHz. The dependence of the feature depth on pulse energy, feed rates, number of consecutive passes over the same area and polarization was investigated. A logarithmic dependence of the groove depth on the laser fluence is observed with two regimes characterized by different ablation rates (at fluences $e \times \Phi_{th}$) and different thresholds: $I_g = 44\text{--}62 \text{ nm/pulse}$ and $\Phi_{th} = 86\text{--}120 \text{ mJ/cm}^2$ in the gentle ablation regime for feed rates ranging from 100 to 500 $\mu\text{m}/\text{s}$ respectively, and $I_s = 144\text{--}100 \text{ nm/pulse}$ and $\Phi_{th} = 460\text{--}320 \text{ mJ/cm}^2$ in the strong ablation regime for feed rates ranging from 100 to 250 $\mu\text{m}/\text{s}$ respectively [51]. The groove depth was found to be inversely proportional to the feed rate or equivalently linearly proportional to the effective number of pulses delivered. The ablation rates, obtained from a linear fit to data measured at constant fluence $\Phi_0 \approx 1900, 650$ and 210 mJ/cm^2 , were $B = 195, 80$ and 50 nm/pulse respec-

tively. With multiple passes over the same groove, the depth increases linearly up to approximately 20 consecutive passes. Above 20 passes ablation rate decreases until a depth limit is reached. The depth limit exhibits a logarithmic dependence with two distinct regimes analogous to single pass cutting. The best results in terms of groove geometry and depth limit were obtained with the polarization of the beam perpendicular to the cutting direction.

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REFERENCES

- See, e.g., A. Gat, J.F. Gibbons: Appl. Phys. Lett. **32**, 142 (1978); R.T. Young, C.W. White, G.J. Clark, J. Narayan, W.H. Christie, M. Murakami, P.W. King, S.D. Kramer: Appl. Phys. Lett. **32**, 139 (1978)
- P.L. Liu, R. Yen, N. Bloembergen, R.T. Hodgson: Appl. Phys. Lett. **34**, 864 (1979)
- J.M. Liu, R. Yen, H. Kurz, N. Bloembergen: Appl. Phys. Lett. **39**, 755 (1981)
- C.V. Shank, R. Yen, C. Hirlmann: Phys. Rev. Lett. **51**, 900 (1983)
- B.N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, A. Tunnermann: Appl. Phys. A **63**, 109 (1996)
- X. Liu, D. Du, G. Mourou: IEEE J. Quantum Electron. **QE-33**, 1706 (1997)
- L. Shah, J. Tawney, M. Richardson, K. Richardson: Appl. Surf. Sci. **183**, 151 (2001)
- D. Ramanathan, P.A. Molian: J. Manufacturing Sci. Eng. **124**, 389 (2002)
- G. Dumitru, V. Romano, H.P. Weter, M. Sentis, W. Marine: Appl. Phys. A **74**, 729 (2002)
- D. Ashkenasi, G. Muller, A. Rosenfeld, R. Stoian, I.V. Hertel, N.M. Bulgakova, E.E.B. Campbell: Appl. Phys. A **77**, 223 (2003)
- S. Adachi: *Properties of InP*, INSPEC p. 416 (1993)
- J. Bonse, J.M. Wrobel, J. Krüger, W. Kautek: Appl. Phys. A **72**, 89 (2001)
- M. Argument, S. Kirkwood, K. Chau, A. van Popta, Y. Tsui, R. Fedosejevs: SPIE **9-10**, 196 (2002)
- J.M. Liu: Opt. Lett. **7**, 196 (1982)
- D. von der Linde, K. Sokolowski-Tinten: Appl. Surf. Sci. **154-155**, 1 (2000)
- A. Borowiec, M. Mackenzie, G.C. Weatherly, H.K. Haugen: Appl. Phys. A **77**, 411 (2003)
- Y. Jee, M.F. Becker, R.M. Walser: J. Opt. Soc. Am. B **5**, 648 (1988)
- J. Guddle, J. Hohlfield, J.G. Müller, E. Matthias: Appl. Surf. Sci. **127-129**, 40 (1998)
- D. Ashkenasi, M. Lorenz, R. Stoian, A. Rosenfeld: Appl. Surf. Sci. **150**, 101 (1999)
- J. Bonse, P. Rudolph, J. Krüger, S. Baudach, W. Kautek: Appl. Surf. Sci. **154-155**, 659 (2000)
- J. Bonse, S. Baudach, J. Krüger, W. Kautek, M. Lenzner: Appl. Phys. A **74**, 19 (2002)
- D. Bäuerle: *Laser Processing and Chemistry*, (Springer-Verlag, Berlin Heidelberg 2000)
- S. Nolte, C. Momma, H. Jacobs, A. Tunnermann, B.N. Chichkov, B. Wellegehausen, H. Welling: J. Opt. Soc. Am. B **14**, 2716 (1997)
- S. Preuss, A. Demchuk, M. Stuke: Appl. Phys. A **61**, 33 (1995)
- E.D. Palik: *Handbook of Optical Constants of Solids*, (Academic Press, San Diego, California 1985)
- W. Kautek, J. Krüger: Mater. Sci. Forum **173-174**, 17 (1995)
- L. Huang, J.P. Callan, E.N. Glezer, E. Mazur: Phys. Rev. Lett. **80**, 185 (1998)
- J. Bonse, J.M. Wrobel, K.W. Brzezinka, N. Esser, W. Kautek: Appl. Surf. Sci. **202**, 272 (2002)
- K. Furusawa, K. Takahashi, H. Kumagai, K. Midorikawa, M. Obara: Appl. Phys. A. **69**, S359 (1999)
- K. Venkatakrishnan, B. Tan, B.K.A. Ngoi: Opt. Laser Technol. **34**, 199 (2002)

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- 31 Y. Hirayama, H. Yabe, M. Obara: J. Appl. Phys. **89**, 2943 (2001)
- 32 Y. Hirayama, M. Obara: J. Appl. Phys. **90**, 6447 (2001)
- 33 D. Ashkenasi, A. Rosenfeld, H. Varel, M. Wahner, E.E.B. Campbell: Appl. Surf. Sci. **120**, 65 (1997)
- 34 M. Lenzner, J. Krüger, S. Sartania, Z. Cheng, C. Spielmann, G. Mourou, W. Kautek, F. Krausz: Phys. Rev. Lett. **80**, 4076 (1998)
- 35 S. Ameer-Beg, W. Perrie, S. Rathbone, J. Wright, W. Weaver, H. Champoux: Appl. Surf. Sci. **127-129**, 875 (1998)
- 36 E.E.B. Campbell, D. Ashkenasi, A. Rosenfeld: Lasers in Materials Science **301**, 123 (1999), R.P. Agrawal ed. (Trans Tech. Publications Ltd. Switzerland, 1999)
- 37 A.E. Wynne, B.C. Stuart: Appl. Phys. A **76**, 373 (2003)
- 38 K. Venkatakrishnan, B. Tan, P. Stanley, L.E.N. Lim, B.K.A. Ngoi: Opt. Eng. **41**(6), 1441 (2002)
- 39 W.M. Steen: *Laser Material Processing* (Springer-Verlag, London 1998)
- 40 N. Barsch, K. Korber, A. Ostendorf, K.H. Tonshoff: Appl. Phys. A **77**, 237 (2003)
- 41 S. Nolte, C. Momma, G. Kamlage, A. Ostendorf, C. Fallnich, F. von Alvensleben, H. Welling: Appl. Phys. A **68**, 563 (1999)
- 42 K. Venkatakrishnan, B. Tan, P. Stanley, N.R. Sivakumar: J. Appl. Phys. **92**, 1604 (2002)
- 43 J. Bonse, M. Geuß, S. Bandach, H. Sturm, W. Kautek: Appl. Phys. A. **69**, S399 (1999)
- 44 M. Prasad, H.E. Ruda, J.J. Dubowski: J. Vac. Sci. Technol. B **15**, 2046 (1997)
- 45 J.M. Wrobel, C.E. Moffitt, D.M. Wieliczka, J.J. Dubowski, J.W. Fraser: Appl. Surf. Sci. **127-129**, 805 (1998)
- 46 R. Matz, H. Weber, G. Weimann: Appl. Phys. A **65**, 349 (1997)
- 47 T.H. Her, R.J. Finlay, C. Wu, S. Delwala, E. Mazur: Appl. Phys. Lett. **73**, 1673 (1998)
- 48 T.H. Her, R.J. Finlay, C. Wu, E. Mazur: Appl. Phys. A. **70**, 383 (2000)
- 49 E. Dupont, X. Zhu, S. Chiu, S. Moisa, M. Buchanan, M. Gao, H.C. Liu, P.B. Corkum: Semicond. Sci. Technol. **15**, 1.15 (2000)
- 50 T. Kim, H.S. Kim, M. Hetterich, D. Jones, J.M. Girkin, E. Bente, M.D. Dawson: Mater. Sci. Eng. **B82**, 262 (2001)
- 51 Note that in our first preliminary work we reported that the data for groove depth versus pulse energy could be fit to a straight line over a substantial fluence range. See: A. Borowiec, H.K. Haugen, CLEO/QELS 2002 Technical Digest, paper CThK37, p. 220, Long Beach, USA, 2002. However with much improved statistics and by including data for low pulse energies, it was found that the results were much better described by the approach outlined in this paper.

The experimental approach presented in this paper is a good starting point for further research. Systematic investigation of the dependence of the ablation rates on the pulse energy (fluence), the feed rate and the number of consecutive passes can be readily extended to include a broader range of laser parameters, such as, different wavelengths, pulse durations, focusing conditions, non-Gaussian beam profiles and different materials.

As an example, several preliminary experiments were repeated following the method outlined in the paper with femtosecond laser pulses centered at the wavelengths of 400 nm. Fig. 5.1 shows the data and the corresponding SEM images of the groove depth dependence on the pulse energy, feed rate and the number of consecutive passes for grooves machined with 400 nm pulses.

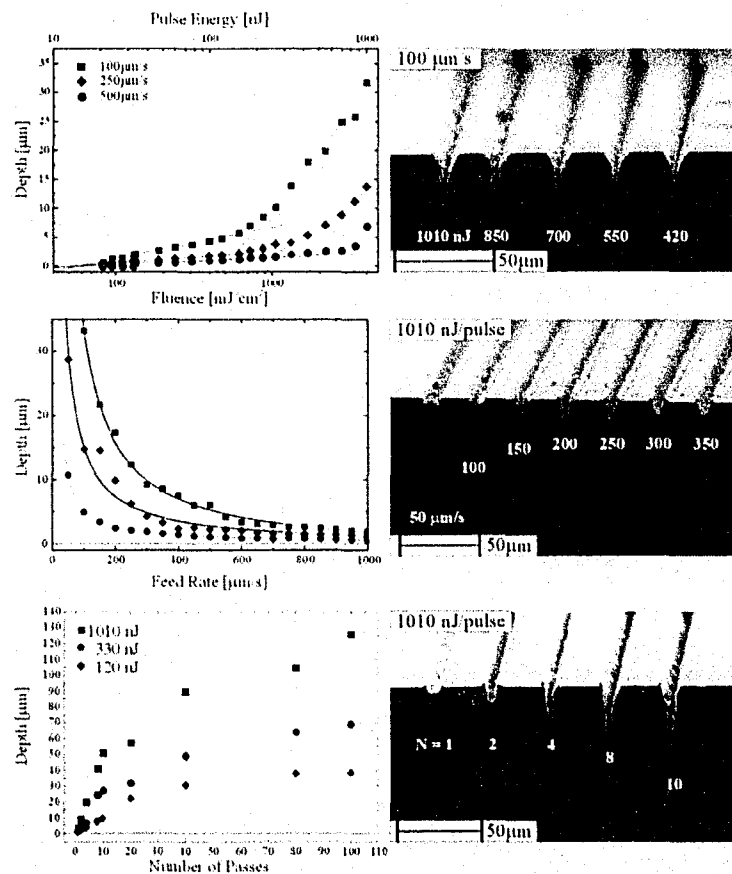


Figure 5.1: Data of laser machining of grooves at 400 nm, showing the dependence of groove depth on fluence (top), feed rate (middle), number of consecutive passes (bottom) and the corresponding SEM images.

The groove depth exhibits a logarithmic dependence on the pulse energy (fluence) with two distinct regimes, characterized by different ablation rates and different thresholds. The measured threshold fluences were approximately two times lower than in experiments done with 800 nm pulses. These preliminary results are consistent with measurements of the wavelength dependence of the ablation threshold presented in

Section 4.3. The groove depth was inversely proportional to the feed rate, scaling as v^{-1} , as found previously in experiments with 800 nm pulses. The measurements of the groove depth as a function of multiple passes also showed similar trends. The groove depth initially increased linearly with an increasing number of passes and eventually a depth limit was approached asymptotically. For grooves machined with 400 nm pulses the depth limit was larger than for grooves machined with 800 nm with the same incident fluence. The aspect ratio of the grooves was also higher and typically the groove geometry and the surface morphology were improved. Generally, the data fits very well to the equations presented in the paper and a similar treatment can be applied in a more detailed analysis.

Micromachining with 400 nm and further extension to UV region would be very relevant for practical applications. As shown in Section 4.3 the ablation threshold decreases with decreasing wavelength, therefore lower pulse energy is required in processing. With an increasing absorption coefficient for shorter wavelengths the energy is deposited in a smaller volume, which leads to improved vertical precision of the machining process. Also the use of 400 nm or UV pulses allows focusing to smaller dimensions and therefore leads to increased lateral precision.

In another example of potential follow up work, the same set of experiments was performed with nanosecond pulses. The results and the corresponding SEM images are shown in Fig. 5.2.

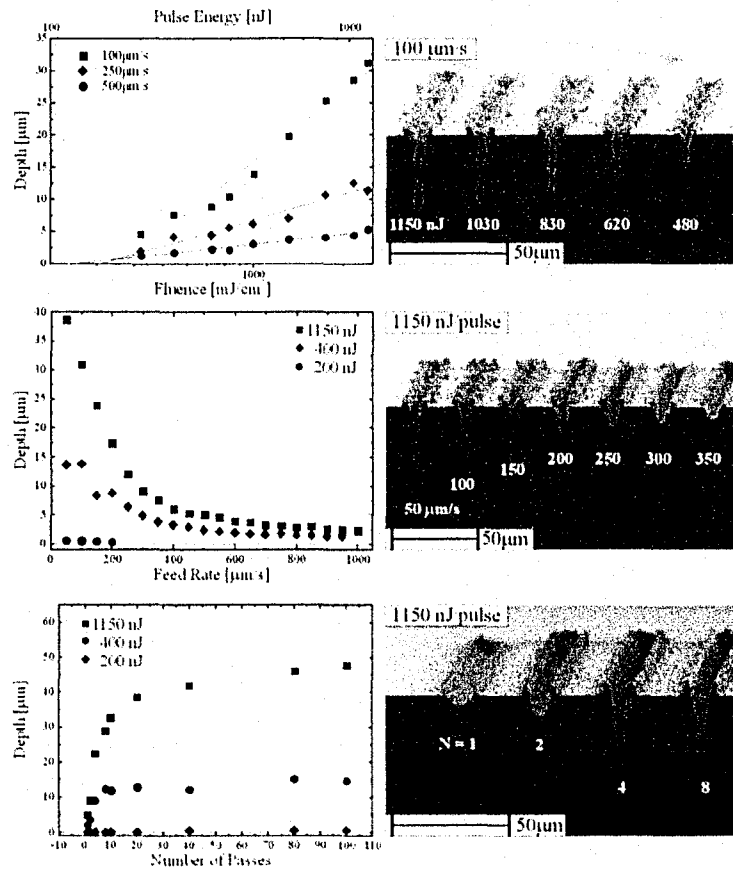


Figure 5.2: Machining of InP with nanosecond pulses

The groove depth exhibits a logarithmic dependence on the pulse energy (fluence). In contrast to femtosecond ablation, only a single regime is observed. The ablation threshold is approximately four times higher in nanosecond ablation compared to femtosecond ablation at the same wavelength. The surface morphology of grooves machined with nanosecond pulses is poor compared to morphology of grooves machined with femtosecond pulses of the same fluence. The burr along the side of the grooves is much more pronounced and typically more surface debris accumulates in the vicinity of the cuts. The advantages of femtosecond laser micromachining are especially evident in machining of deep grooves with multiple laser passes over the same groove. For the same pulse energy, the depth limit of grooves machined with nanosecond pulses is approximately half the value obtained in femtosecond micromachining. The depth limit is also reached significantly faster. A drop in the ablation rate is already observed after eight passes for similar laser fluence.

Although femtosecond micromachining offers substantial advantages over machining with nanosecond pulses, ultrafast lasers are more expensive and complicated compared to the well established nanosecond laser technology. In non-critical applications the use of nanosecond or picosecond lasers, especially operating in the UV wavelength range, can lead to satisfactory results at significantly reduced cost. Therefore,

analysis of the parameter space for nanosecond laser machining can prove to be equally important.

Finally, all experiments presented and proposed in this section can be extended to the analysis of other materials. Recently, Crawford *et al.* [98] presented results of femtosecond laser micromachining of Si performed under similar conditions. Systematic investigation of laser micromachining of various materials in conjunction with theoretical analysis will lead to a better understanding of the ablation process. With a good understanding of the underlying physics it should be possible to predict many aspects of micromachining of various materials by considering their optical and physical properties. Based on purely technological interest, cataloging of the machining parameters will provide a useful reference for the emerging applications in laser micromachining.

Another interesting extension of the research presented in this paper is three dimensional structuring accomplished by varying the angle of incidence of the laser beam relative to the sample surface. This approach allows machining of grooves at arbitrary angles. Fig. 5.3 shows an example of grooves cut with 1 μ J, 130 fs pulses, 100 passes/groove at feed rate of 500 μ m/s and sample tilts of 0°, 20°, 40° and 60°.

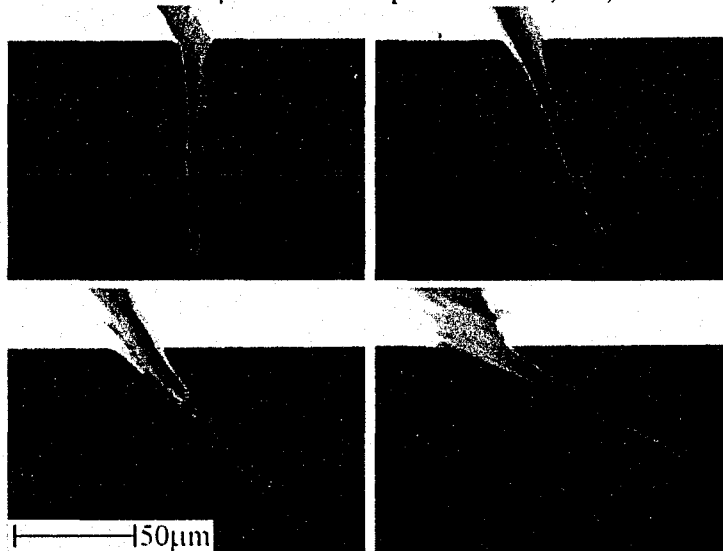


Figure 5.3: Grooves machined in InP with pulse energy of 1000 nJ/pulse, 1kHz at 500 μ m/s, 100 passes/line with laser beam at 0°, 20°, 40°, 60° relative to the sample surface. The samples were processed in ambient atmosphere.

This technique allows either efficient removal of macroscopic amounts of material or fabrication of free standing or suspended structures. Fig. 5.4 shows a v-groove and a partially suspended beam micromachined by making two incisions at 45°. This is a unique and potentially valuable method, as fabrication of similar structures would be difficult by conventional semiconductor processing techniques, such as, wet or dry etching. The machining was performed at ambient pressure. It is interesting to note that the groove depth is virtually the same as in grooves machined under rough vacuum. The ability to fabricate such structures at atmospheric pressure is particularly important in the industrial setting due to the high cost of vacuum equipment. Femtosecond laser

micromachining provides a flexible, single step tool for machining of structures shown in Fig. 5.3 and 5.4.

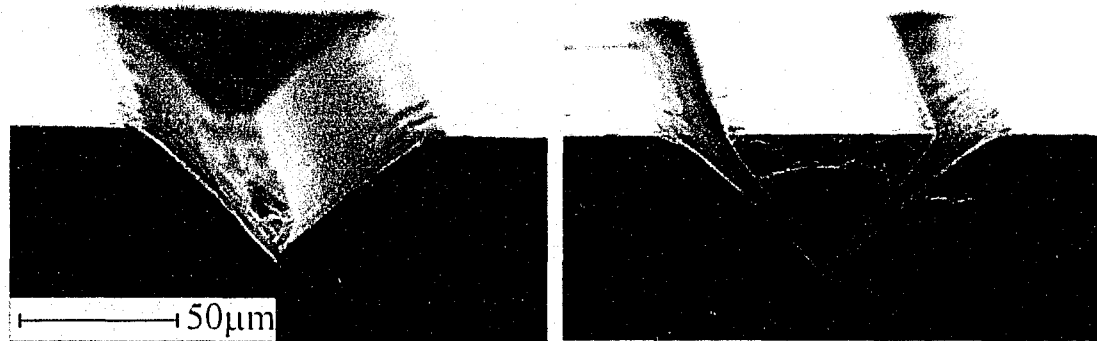


Figure 5.4: V-groove and a partially suspended beam machined by making two incisions at 45° machined under ambient atmosphere.

5.3 Paper 5 – Imaging the strain fields resulting from laser micromachining of semiconductors

This paper presents the measurements of strain fields in the vicinity of grooves micromachined in InP by femtosecond and nanosecond laser pulses. The measurements were performed by a spatially and polarization resolved photoluminescence imaging technique, commonly known as degree of polarization (DOP), developed in Dr. Daniel Cassidy's group at McMaster University. The results presented in this paper report the first use of the DOP technique in analysis of laser micromachined structures. In this study, the analysis was performed on two grooves micromachined with ≈ 8 ns and ≈ 130 fs pulses of equal fluence ~ 2 J/cm². A simple finite element model was developed to help interpret the data.

Dr. Doug Bruce performed all DOP scans and Dr. Daniel Cassidy provided support and input on the manuscript preparation, and valuable discussion. I would like to acknowledge Dr. Mark Fritz for helpful discussions of the DOP technique and for help with the data analysis. Also, I would like to thank Dr. Jan Thøgersen for encouragement for my completion of this work.

Imaging the strain fields resulting from laser micromachining of semiconductors

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The residual strain fields resulting from laser micromachining of grooves in indium phosphide with femtosecond and nanosecond light pulses are analyzed using a spatially resolved degree-of-polarization photoluminescence technique. Significant differences in the geometry of the strain patterns are observed in grooves machined by femtosecond and nanosecond pulses. For the specific conditions investigated, the sign of the degree of polarization signal is opposite in the two cases indicating that areas under tension in femtosecond machined samples are under compression in nanosecond machined samples and visa versa. The experimental data are compared with results from a finite element model. © 2003 American Institute of Physics. [DOI: 10.1063/1.1591241]

The potential of femtosecond lasers as a materials processing tool has been demonstrated by many groups (see, e.g., Refs. 1–5). Many future applications may depend critically on the quality of the machined materials in terms of collateral damage, residual strain, and localized changes in optical, mechanical, and electronic material properties. In this work, we characterize laser-machined semiconductor samples, utilizing the degree-of-polarization (DOP) photoluminescence (PL) technique,^{6,7} supported by scanning electron microscopy and finite element modeling (FEM).

The micromachining experiments were performed with a commercial, regeneratively amplified, Ti:Sapphire laser operating at a center wavelength of 800 nm. The laser emitted linearly polarized light pulses of 130 fs duration at a 1 kHz repetition rate. Nanosecond pulses were obtained from the same laser by blocking the seed pulse to the amplifier and bypassing the compressor. N-doped (100) InP wafers were placed in a small vacuum chamber mounted on a computer controlled xyz translation stage and experiments were performed under a rough vacuum of ~ 0.1 mbar. The laser was brought in perpendicular to the (100) surface and focused on the sample by a 5 $\times$ microscope objective (Newport 5 $\times$ -M). The spot size (w_0 at $1/e^2$) at the focal point was measured by the method described by Liu⁸ and determined to be ~ 5.5 μm . In the experiments, sets of grooves were machined in InP samples with 130 fs and 7 ns pulses with pulse energies of about 1 μJ (fluence of ~ 2 J/cm²) and a feed rate of 250 $\mu\text{m/s}$. After machining, the samples were cleaved perpendicular to the grooves and examined with a scanning electron microscope (SEM). The cross sections were subsequently imaged by the DOP technique.

The method of strain measurements using the DOP technique is based on an analysis of the polarization state of a luminescent signal. The details of the technique can be found elsewhere.^{6,9} Briefly, a low power 633 nm helium–neon laser beam is reflected from a cold mirror and focused on the

sample facet by a 40 $\times$ microscope objective. The luminescence is collected with the same objective in a confocal arrangement and passes through the cold mirror, a filter which removes residual HeNe light, and finally through a polarizer. The polarizer is continuously rotated with the rotation synchronized with the detection system such that signals L_x and L_y as well as L_{xy} and L_{-xy} can be recorded. Signals designated as L_x , for example, correspond to the photoluminescence (PL) signal collected with the polarizer aligned along the x axis. The coordinate system is shown in Fig. 1. The DOP signal is related to the luminescence signals measured in the two orthogonal polarizations (L_x, L_y) by

$$\rho_{\text{DOP}} = \frac{L_x - L_y}{L_x + L_y} = K_0(\sigma_{xx} - \sigma_{yy}) \quad (1)$$

where K_0 is a calibration constant ($9.4 \pm 0.1 \times 10^{-11}$ cm² dyn⁻¹ for InP) and σ_{xx} and σ_{yy} are the stresses in the x and y directions.⁶ Since the facet under investigation is a free surface, stress in the z direction is zero, i.e., $\sigma_{zz} = 0$. The rotated degree of polarization (ROP) signal is related to the luminescence signals in the two orthogonal polarizations (L_{xy}, L_{-xy}) by

$$\rho_{\text{ROP}} = \frac{L_{xy} - L_{-xy}}{L_{xy} + L_{-xy}} = 2 \cdot K_0 \sigma_{xy} \quad (2)$$

where σ_{xy} are the shear stresses. Two-dimensional images are obtained by scanning the sample past the stationary objective under computer control. At each point, values of L_x , L_y and L_{xy} , L_{-xy} are recorded and values of the DOP and ROP signals are calculated according to Eqs. (1) and (2), respectively. A strain resolution of $> 10^{-5}$ and a spatial resolution of ~ 1 μm have been demonstrated.⁶

Figure 1 shows SEM, spatially resolved PL (PL = $L_x + L_y$), DOP, and ROP images of two grooves machined in InP with 130 fs and 7 ns pulses. The feature created with femtosecond pulses exhibits significantly better morphology. Debris found in the vicinity of the cut can be easily removed with lens tissue and methanol or an ultrasonic bath. The typical depth of grooves machined with the specified set of parameters is ~ 5 μm . The trenches formed with nanosecond

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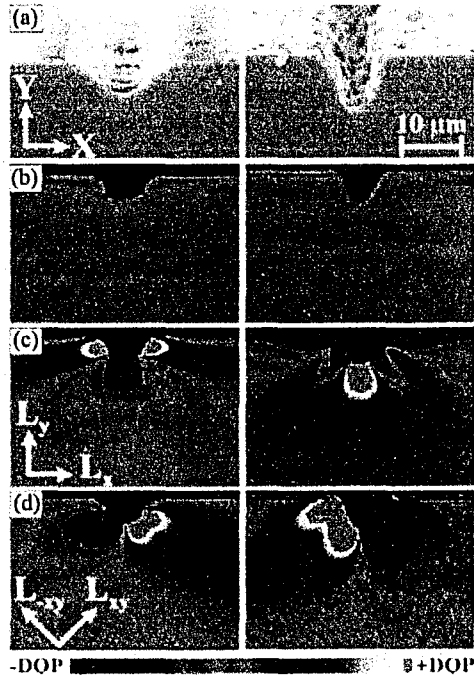


FIG. 1. (Color) (a) SEM, (b) spatially resolved PL ($PL = L_x + L_y$), (c) DOP, and (d) ROP images of grooves cut with 130 femtosecond (left-hand side) and 7 nanosecond (right-hand side) laser pulses, centered around 800 nm, repetition rate of 1 kHz and cutting speed of 250 $\mu\text{m/s}$.

pulses are typically around 10 μm deep, are generally less uniform and leave a significant amount of debris. Spatially resolved PL [Fig. 1(b)] shows a uniform intensity across both facets and virtually no PL quenching even in the close vicinity of the cuts. Polarization resolved PL [Fig. 1(c)] reveals the residual material strain. The patterns are very symmetric and reproducible; however, there are substantial differences between the DOP images of grooves cut with fs- and ns-duration laser pulses. In addition to DOP pattern differences, the signs of the DOP and ROP signals are reversed in the images corresponding to the two pulse durations. The areas which are in tension ($DOP < 0$) in femtosecond-machined grooves are in compression ($DOP > 0$) in nanosecond-machined grooves. The DOP signal, directly beneath the trench machined with femtosecond pulses, was found to be $\rho_{DOP} \sim -16\%$ and dropped to background value $\rho_{DOP} \sim 0\%$ at a distance of 20 μm . In grooves machined with nanosecond pulses, the maximum value of the DOP signal was measured to be $\rho_{DOP} \sim +12\%$, and dropped to the background level over a distance of 30 μm . The functional dependence of the DOP and ROP signals on various machining parameters, such as pulse energy, feed rate, wavelength, and the pulse duration will be subjects of future investigations.

Determining the absolute values of the stress components is not straightforward since the DOP signal is proportional to the difference between stresses in the x and y directions. For example, a DOP value of $\rho_{DOP} = -16\%$

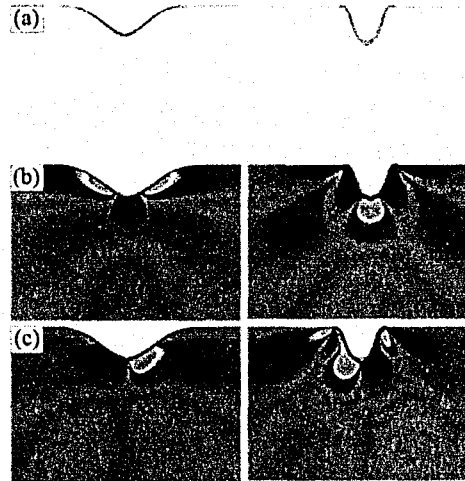


FIG. 2. (Color) Finite element modeling of trenches cut with (left-hand side) femtosecond and (right-hand side) nanosecond pulses: (a) Geometry of the model, (b) simulated DOP image, and (c) simulated ROP image.

corresponds to $(\sigma_{xx} - \sigma_{yy}) = 170 \text{ MPa}$. (It should be noted that the maximum values of the strain are close to the expected limit of linearity.)⁶ Without modeling or symmetry, it is difficult to predict which stress component, σ_{xx} or σ_{yy} , is dominant. In the case of the ROP, extracting quantitative information is easier since the ROP signal is directly proportional to the shear stress.

It is reasonable to expect the amount and composition of the resolidified material inside the trench to play a key role in determining the nature and magnitude of the residual stresses. Transmission electron microscopy (TEM)¹⁰ analysis of features on InP ablated in vacuum by femtosecond pulses reported a substantial amount of polycrystalline surface material. Micro-Raman analysis of femtosecond ablation of InP (Ref. 11) in air was also reported recently. In Ref. 11, a number of different morphological regions were observed after single and double femtosecond pulse irradiation, including amorphous and polycrystalline regions. Our process of cutting trenches is different, being equivalent to irradiation of the same spot by ~ 40 pulses. The micro-Raman experiments¹¹ enabled observations of both compressive and tensile stress regions, with absolute values in the range of hundreds of MPa. Although the higher single pulse fluences reported in Ref. 11 were similar to our experimental conditions, the micro-Raman analysis is sensitive to a depth of tens of nanometers. Our analysis probes stress values in the vicinity of the groove on a depth scale of microns—hence the two approaches are complementary.

Analogous works on nanosecond ablation of InP are not available. Amer *et al.*¹² reported micro-Raman analysis of Si wafers micromachined with ns-duration excimer lasers. In Ref. 12, the authors observed high average tensile stresses $\sim 0.8 \text{ GPa}$ induced as a result of laser machining as well as a significant amorphization of the surface. In ns-laser machining of compound semiconductors, the loss of the more volatile component routinely occurs. Machining of InP is ex-

pected to lead to an In-rich surface, which could cause stresses in the underlying material. The differences between the resolidified surface layers, combined with possible differences in defect types and densities in the nearby bulk solid, might explain the reversal of the polarity of the ns and fs DOP signals seen in Fig. 1. The mechanism leading to this difference is still an open question.

To further explore the effects of the resolidified layer on the residual stress in the vicinity of laser-machined trenches, we have developed a simple FEM using the commercial software package FEMLAB®. The geometry of the model is shown in Fig. 2(a). It consists of an InP substrate with a machined groove that is lined with a layer of solidified material. In our calculations, the solidified layer was brought to 300 K, the same temperature as the substrate, from an initial temperature of 1300 K (roughly the melting temperature of InP). Upon freezing, the thermal mismatch results in a strained interface. The required physical effects were artificially simulated by using a positive thermal expansion coefficient of the melt zone for ns-pulse irradiation, and a negative value for fs-pulse machining. Figures 2(b) and 2(c) show simulations of the DOP ($\sigma_{xx} - \sigma_{yy}$) and the ROP (σ_{xy}) images of a machined groove with pulses in the respective temporal domains.

Although the match between the experimental and simulated images is not exact, the results of this very simple model display similar stress patterns to those seen in Fig. 1. The shapes of the simulated DOP and ROP patterns were found to be sensitive to the size and geometry of the resolidified layer as well as the initial temperature assumed for the melt zone. To develop a more sophisticated model, the details of the geometry and the composition of the resolidified layer are needed, as well as a defect analysis in the nearby bulk. Cross-sectional TEM studies of these structures would be an excellent supplement to the DOP technique, and such studies are currently being planned. A good example of this approach was demonstrated in the analysis and modeling of quantum wires grown in V grooves on InP substrates¹³ where TEM, DOP, and FEM were used in an investigation.

The initial temperature of the melt zone can be calculated from the considerations of the energy deposited in the material. Bäuerle¹⁴ provides a comprehensive overview of theory and experiments for nanosecond laser processing of materials. Reference 14 also gives an overview of the progress on femtosecond studies, although the theory of femtosecond laser-materials interactions is still the subject of intensive theoretical and experimental investigations. Many models have been proposed to explain various aspects of the ultrafast ablation process.^{15–18} Also, a theory of defect-strain instability and the formation of periodic surface relief in semiconductors irradiated with femtosecond pulses has been recently published.¹⁹ The DOP technique would provide a good method of testing various models, leading to a better understanding of the underlying physics. Detailed modeling

would also enable extraction of the values of the stresses in the orthogonal directions.

In conclusion, with the advances in ultrafast laser micro-machining, there is a need for microanalysis tools. The DOP technique is a simple and effective tool in strain analysis of direct band-gap semiconductors, which are the backbone of the optoelectronics industry. The present study provides an analysis of both the PL efficiency and the residual stress resulting from femtosecond laser micromachining, and over length scales relevant to device applications. Since both the magnitude and the sign of the stress could sensitively depend on some of the machining conditions, an investigation of a broad range of parameters will be required to develop a comprehensive picture. Our evidence suggests that the amount and nature of the resolidified material may be a key determinant in producing residual strain. Further detailed microscopic analysis is required to support more sophisticated models, which are needed to extract the values of stress in the two orthogonal directions and gain a better understanding of the underlying physics.

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- ¹X. Liu, D. Du, and G. Mourou, *IEEE J. Quantum Electron.*, **33**, 1706 (1997).
- ²B. N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, and A. Tünnermann, *Appl. Phys. A: Mater. Sci. Process.*, **63**, 109 (1996).
- ³T. Kim, H. S. Kim, M. Hettenich, D. Jones, J. M. Gorkin, E. Bente, and M. D. Dawson, *Mater. Sci. Eng., B*, **82**, 262 (2001).
- ⁴D. Ramanathan and P. A. Mohan, *J. Manuf. Sci. Eng.*, **124**, 389 (2002).
- ⁵G. Dumutur, V. Romano, H. P. Weber, M. Sentis, and W. Manne, *Appl. Phys. A: Mater. Sci. Process.*, **74**, 729 (2002).
- ⁶P. D. Colbourne and D. I. Cassidy, *IEEE J. Quantum Electron.*, **29**, 62 (1993).
- ⁷J. Yang, B. B. Flenkig, D. I. Cassidy, D. M. Bruce and I. M. Templeton, *Semicond. Sci. Technol.*, **10**, 483 (1995).
- ⁸J. M. Liu, *Opt. Lett.*, **7**, 196 (1982).
- ⁹D. T. Cassidy, *Mater. Sci. Eng., B*, **91–92**, 2 (2002).
- ¹⁰A. Borowiec, M. MacKenzie, G. C. Weatherly, and H. K. Haugen, *Appl. Phys. A: Mater. Sci. Process.*, (to be published).
- ¹¹J. Bonse, J. M. Wrobel, K. W. Brzezinka, N. Esser, and W. Kaulek, *Appl. Surf. Sci.*, **202**, 272 (2002).
- ¹²M. S. Amer, L. Dosser, S. Leclair, and J. F. Maguire, *Appl. Surf. Sci.*, **187**, 291 (2002).
- ¹³A. Gupta, G. C. Weatherly, D. T. Cassidy, and D. M. Bruce, *J. Appl. Phys.*, **82**, 6016 (1997).
- ¹⁴D. Bäuerle, *"Laser Processing and Chemistry"* 2nd ed. (Springer, Berlin, 2000).
- ¹⁵S. I. Anisimov, N. A. Inogamov, A. M. Oparin, B. Rethfeld, I. Yabe, M. Ogawa, and V. E. Fortov, *Appl. Phys. A: Mater. Sci. Process.*, **69**, 617 (1999).
- ¹⁶N. A. Inogamov, Yu. V. Petrov, S. I. Anisimov, A. M. Oparin, N. V. Shaposhnikov, D. von der Linde, and J. Meyer-ter-Vehn, *JETP Lett.*, **69**, 310 (1999).
- ¹⁷S. Stano, R. Pini, and R. Salimbeni, *Appl. Phys. Lett.*, **74**, 1233 (1999).
- ¹⁸R. E. W. Herrmann, J. Gerlach, and E. E. B. Campbell, *Appl. Phys. A: Mater. Sci. Process.*, **66**, 35 (1998).
- ¹⁹V. I. Emel'yanov and D. V. Babak, *Appl. Phys. A: Mater. Sci. Process.*, **74**, 797 (2002).

As demonstrated in the paper, the DOP imaging technique is a powerful tool for evaluation of laser micromachined structures in direct bandgap semiconductors. The results presented in this paper can serve as an excellent starting point for further research. The natural continuation of the work presented would include a systematic study of the strain fields resulting from micromachining of InP using a broader range of laser parameters. As an example, Fig. 5.5 shows a set of SEM, DOP and ROP images of grooves micromachined by 130 fs pulses, at a feed rate of 250 $\mu\text{m/s}$ and pulse energies varying from 1100 to 230 nJ/pulse.

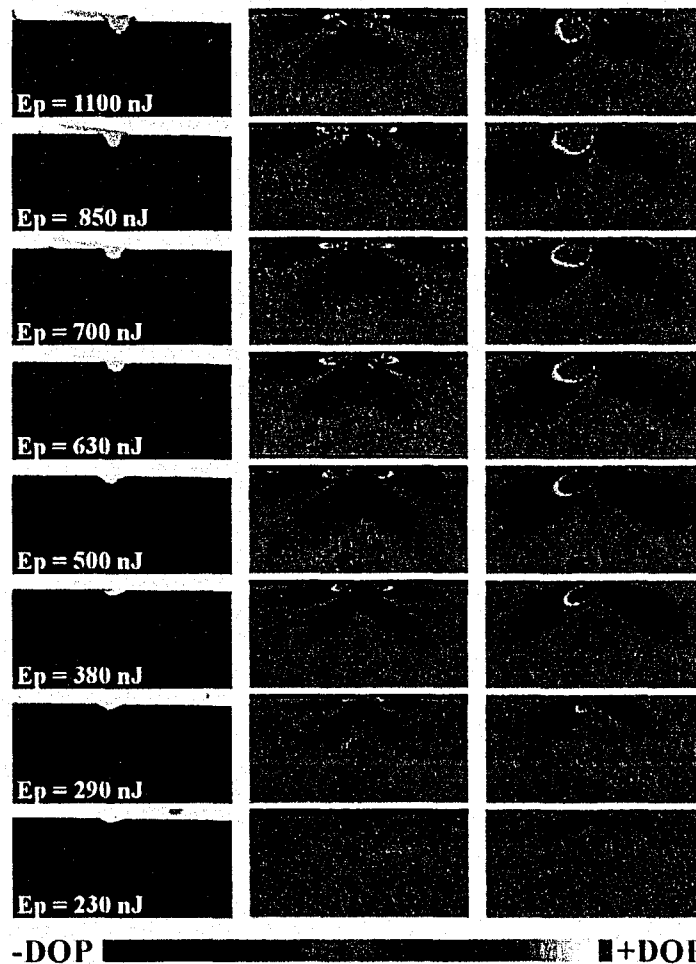


Figure 5.5: SEM (left), DOP (middle) and ROP (right) images of grooves micromachined by 130 fs pulses, at a feed rate of 250 $\mu\text{m/s}$ and with pulse energies varying from 1100 to 230 nJ/pulse.

Qualitative inspection reveals changes in the extent and the geometry of the strain fields with decreasing pulse energy. In a quantitative analysis, one can consider the dependence of the magnitude of the DOP signal on the pulse energy. For example, Fig. 5.6 shows the average value of DOP signal as a function of depth beneath the groove cut with pulse

energy of 700 nJ. Two yellow horizontal lines in the insert indicate the portion of the data averaged.

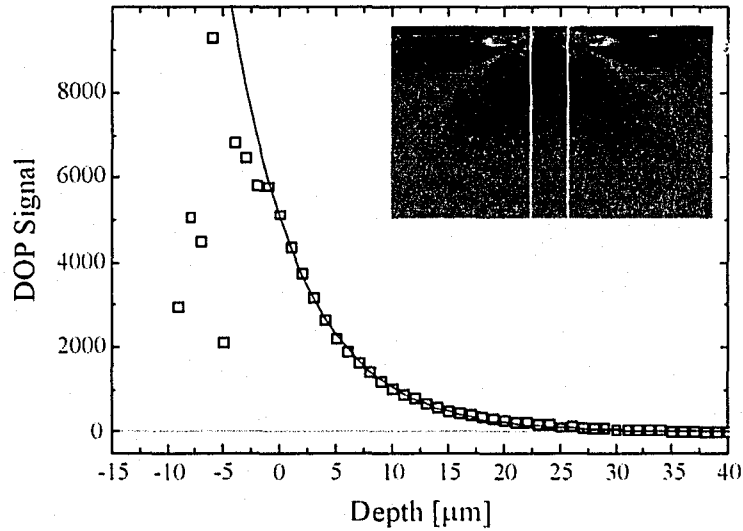


Figure 5.6: Plot of the average value of the DOP signal beneath groove machined with 700 nJ pulses. The two yellow lines in the DOP image in the insert indicate the averaged data.

The data fits very well to an exponential decay equation of the form

$$DOP_{fit}(y) = DOP_o \cdot \exp(-y / Y_o), \quad (5.1)$$

where DOP_o and Y_o are the empirical fit parameters. The parameter DOP_o reflects the peak value of the DOP signal beneath the groove and Y_o represents the characteristic distance over which the DOP signal drops off to e^{-1} of the peak value. The first few data points in Fig. 5.6 correspond to the scan area where the material was removed and hence do not represent a real signal. The points included in the fit were those for which the total photoluminescence yield was approximately constant. Fig. 5.7 shows the dependence of Y_o parameter on the pulse energy. As expected Y_o decreases with decreasing pulse energy although the functional dependence is not obvious at this point.

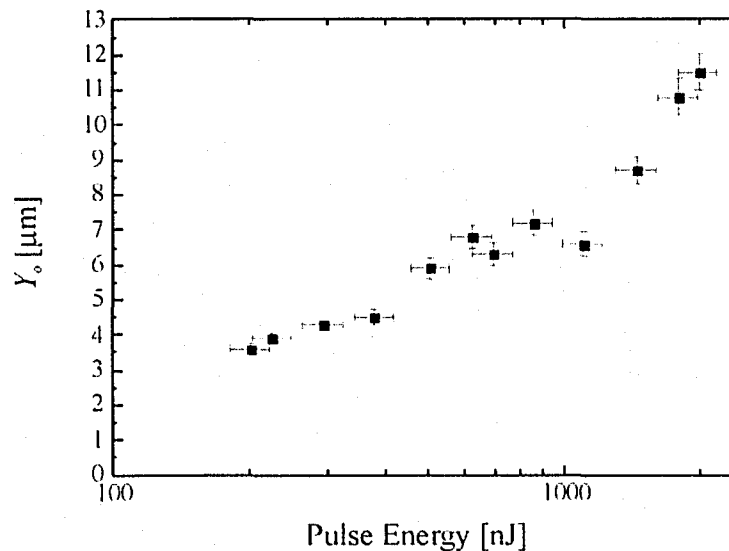


Figure 5.7: Plot of Y_o parameter as a function of pulse energy.

The second obvious area for subsequent research involves detailed theoretical and finite element modeling (FEM). The method proposed is a good starting point for quantitative investigation, however more theoretical work will be required to establish the physical significance of the fit parameter. More sophisticated modeling in conjunction with iterative fitting to the experimental data would also enable extracting the values of the stresses in the orthogonal directions.

Lastly this publication has already stimulated the interest of other research groups studying micro Raman spectroscopy and x-ray topology imaging leading to the initiation of a collaboration with Dr. Patrick J. McNally from the Research Institute for Networks & Communications Engineering (RINCE), Dublin City University in Ireland. As a first step in the collaboration several samples were prepared under the same conditions as presented in the above publication and sent for analysis by micro-Raman spectroscopy and synchrotron x-ray topography. Fig. 5.8 shows an example of preliminary measurements on a groove cut with ≈ 130 fs, 1 μ J pulses at 500 μ m/s, courtesy of Dr. McNally and X. Lu. Micro-Raman spectra correspond to the six locations indicated in the micrograph. Analysis of the Raman data allows one to deduce the composition of the layer and measurements of the stresses in the surface layers. Preliminary conclusions indicate that an amorphous InP phase is located inside the groove and the depth of this layer is less than 100 nm. For probe spots 1 to 4, two crystalline phases were identified beneath the surface. The upper phase is amorphous InP and the lower phase is recrystallized polycrystalline InP with a grain size around 4 nm. The thickest amorphous InP layer and the finest polycrystalline phase are located at probe spot 3 instead of the center of the groove. The highest mechanical stress inside the polycrystalline phase and single-crystalline phase appears to be located at position 2 instead of the center of the groove and there appears to be both tensile and compressive strain inside the groove. It

should be noted that the Raman measurements are sensitive to a rather thin surface layer, typically on the order of the light extinction depth of the excitation source.

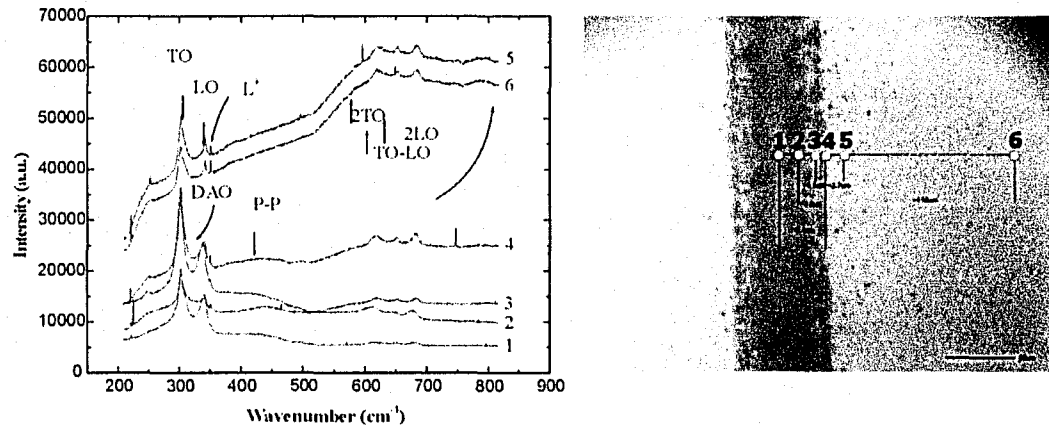


Figure 5.8 (left) InP micro-Raman spectra at 6 selected positions, scan time=150 s, (right) OM image showing micro-Raman probe spot distribution around groove #1.

Additional Raman measurements of the cleaved facet are also planned. The results of the Raman measurements will be compared to DOP measurements and cross-sectional TEM analysis.

5.4 Paper 6 – Sub-surface damage in indium phosphide caused by micromachining of grooves with femtosecond and nanosecond laser pulses

This paper presents cross-sectional TEM analysis of grooves machined in InP with femtosecond and nanosecond laser pulses. The key point of interest was investigation of the microstructure of grooves machined in the two temporal domains and it is a follow up to the work presented in Section 5.3. The DOP images acquired revealed striking differences in the geometry and polarity of the strain fields resulting from machining with femtosecond and nanosecond pulses. The simple finite element model of the grooves revealed that the geometry and composition of the resolidified layer are likely responsible for the observed strain fields. The test of this hypothesis required the knowledge of the extent and composition of the resolidified layer. The cross sectional TEM is the best method for detailed investigation of the microstructure of the ablation features as discussed in Section 4.2.

One problem with the TEM analysis is sample preparation as it requires preparation of electron transparent foils several tens of microns long. Such specimens are very difficult to prepare by standard techniques and requires the use of focused ion beam milling (FIB). In this first study, two grooves machined with femtosecond pulses and two grooves machined with nanosecond pulses were selected for TEM examination. One of the key findings was the observation of a large networks of defects formed under grooves machined with femtosecond pulses. This finding is contrary to previous TEM analysis of single pulse ablation measurements presented in Section 4.2 and the often made claims that femtosecond laser ablation leads to essentially damage free machining.

This work was performed in close collaboration with the Brockhouse Institute for Materials Research (BIMR) at McMaster University. Dr. Martin Couillard and Dr. Gianluigi Botton performed all electron microscopy work and defect analysis. Dr. Martin Couillard also wrote sections of the manuscript dealing with the electron microscopy and the defect analysis. L. Weaver and M. W. Phaneuf at Fibics Ottawa, Canada performed the TEM sample preparation by FIB.

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Sub-surface damage in indium phosphide caused by micromachining of grooves with femtosecond and nanosecond laser pulses

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ABSTRACT Grooves laser-micromachined in InP using 130 fs and 8 ns pulses with fluences ≈ 2 and 0.7 J/cm^2 are investigated by cross-sectional transmission electron microscopy. At the fluence of 2 J/cm^2 , irradiation with both femtosecond and nanosecond laser pulses yield substantial resolidified layers with a maximum thickness of $\approx 0.5 \mu\text{m}$. In contrast, at the fluence of 0.7 J/cm^2 , irradiation with nanosecond pulses leads to a layer of similar thickness, while femtosecond irradiation produces laser induced periodic surface structures with minimal resolidified material. For both fluences, femtosecond pulses generate substantial densities of defects extending over a few microns in depth, while nanosecond laser irradiation leads to no observable damage beneath the resolidified layer. The high peak power density and the stress confinement obtained from femtosecond pulses, along with incubation effects, are identified as the major factors leading to the observed plastic deformations.

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During the past decade the potential of femtosecond laser pulses as a material processing tool has been demonstrated by many groups [1]. It has been shown that material micro-processing with ultrashort laser pulses offers substantial advantages over machining with conventional lasers, leading to improved surface morphology and a reduction in the heat affected zones. Analytical techniques used to assess the final state of material most often included optical, scanning electron, and atomic force microscopy, and, therefore, are only sensitive to changes in the surface morphology. Transmission electron microscopy (TEM) is an ideal tool for probing the material microstructure in the vicinity of the machined features. However, due to difficulty in TEM sample preparation, it is not commonly used. Several groups have reported

TEM analysis of various materials machined by nanosecond and femtosecond lasers, for example metals [2–4], dielectrics [5, 6] and semiconductors [2, 7–9]. In this letter we present results of cross sectional TEM studies of grooves micromachined in indium phosphide (InP) by femtosecond and nanosecond laser pulses that complement recently reported results of strain analysis by a degree of polarization analysis [10]. In particular, we report on damage induced by femtosecond laser irradiation of InP, a compound semiconductor of technological significance for photonics applications.

The micromachining experiments were performed with a commercial, regeneratively amplified Ti:sapphire laser operating at a center wavelength of $\approx 800 \text{ nm}$ and 1 kHz repetition rate. The laser beam was focused on the sample

surface by a $5\times$ microscope objective to a spot size of $5.5 \pm 0.5 \mu\text{m}$ (Gaussian beam radius at $1/e^2$). A set of four grooves were machined in (100) n-InP samples, S doped $\sim 10^{18} \text{ cm}^{-3}$, along the [011] direction with pulses of approximately 130 fs and 8 ns in duration. Pulse energies of ≈ 1.0 and $0.35 \mu\text{J}$ were utilized, at a feed rate of $500 \mu\text{m/s}$, with a beam linearly polarized perpendicular to the cutting direction. After laser machining of grooves the cross sectional TEM samples were prepared by the focused ion beam (FIB) technique as described in [11]. The specimens, coated with a protective platinum and, subsequently, tungsten layer, were milled using 50 keV gallium atoms. The “lift-out” technique was employed whereby the electron transparent foil was cut free by the FIB for stand-alone examination. The TEM work was performed with a JEOL 2010F electron microscope operated at 200 kV and equipped with an energy dispersive X-ray spectrometer (EDS) and a Gatan imaging filter (GIF).

Figure 1 shows a montage of TEM images of a groove cut in InP with $1 \mu\text{J}$ ($\approx 2 \text{ J/cm}^2$), 8 ns pulses. The groove is approximately $4 \mu\text{m}$ deep and the distinct region of resolidified material can be seen on top of the unaffected substrate. The thickness of this layer varies from around 550 nm at the bottom of the groove to slightly less than 200 nm on the side. Droplet shaped particles associated with redeposited materials are observed on the surface of the groove. Significant burrs of $1\text{--}1.5 \mu\text{m}$ in height are also formed around the cut by what appears to be a liquid phase expulsion

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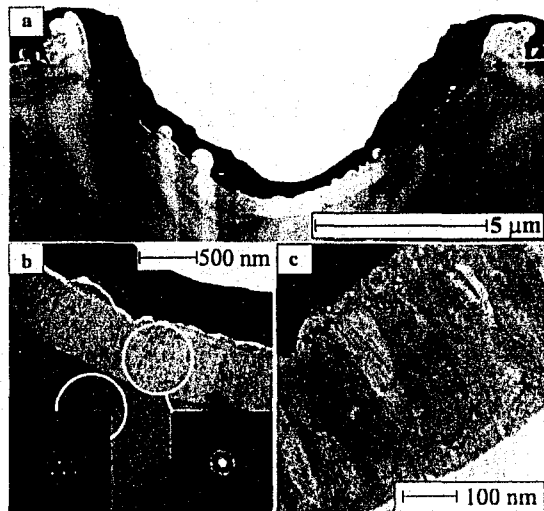


FIGURE 1 Cross sectional TEM images of a groove machined in InP with nanosecond pulses (1 μ J, 8 ns). a Low-resolution view b TEM image and diffraction patterns taken near the bottom of the groove c bright-field scanning TEM close-up of the resolidified layer. The black layer in the images is the protective tungsten layer

process. Figure 1b shows a detailed view of a portion of the resolidified layer near the bottom of the groove. The layer consists of polycrystalline regions of InP, as can be seen from the diffraction pattern, with some In-rich particles identified using EDS. In addition to the large crystals directly visible in the bright-field images there are broader rings in the diffraction pattern suggesting the presence of nanocrystalline material within the resolidified layer. Quantitative determination of the relative fraction of the nanocrystalline resolidified material is presently under investigation. Further analysis to detect whether additional amorphous material is present is also in progress. No evidence of extended defects or microcracking was found below the groove and the diffraction pattern for this region (Fig. 1b) corresponds to the zinc blende structure oriented along the [011] zone axis.

The cross section of the groove (not shown), cut in InP with 8 ns pulses of 350 nJ (≈ 0.7 J/cm²), qualitatively resembles the groove machined with higher energy pulses. The groove is approximately 1.8 μ m deep and lined with ≈ 500 nm of resolidified material. The resolidified InP layer, comprised of significant polycrystalline content, is not very uniform and exhibits a slow spatial frequency modulation in the form

of layers parallel to the groove surface. Burrs of the order of 1 μ m in height are also observed on the side of the groove, and no trace of extended defects are visible beneath the cut.

Figure 2 shows a montage of TEM images of a groove cut in InP with 1 μ J (≈ 2 J/cm²), 130 fs pulses. The groove is approximately 1.8 μ m deep, shallower than its nanosecond counterpart. The resolidified layer is still present

and its thickness varies from around 550 nm at the bottom of the groove to slightly less than 300 nm on the side of the groove. The burr is not as pronounced as in the nanosecond case. The microstructure of the resolidified layer includes polycrystalline grains of InP with some In-rich particles. Analogous to the nanosecond irradiation case, evidence for nanocrystalline content was found in the resolidified layer. The most striking feature is the presence of extended defects beneath the resolidified layer. This highly heterogeneous plastic deformation consists of microtwins, mainly observed at the bottom of the trench, and two dense networks of dislocations present on both sides of the groove and extending 3 μ m beneath the resolidified layer.

Figure 3 shows a montage of TEM images of a groove cut in InP with 350 nJ (≈ 0.7 J/cm²), 130 fs pulses. The groove is approximately 1 μ m deep and laser induced periodic surface structures (LIPSS) are visible features. The spatial period of LIPSS in this regime is typically 600–700 nm. There is very little resolidified material and most of it appears to be on top of the LIPSS in the central part of the groove (Fig. 3b), whereas other modulations in the LIPSS are unaffected (Fig. 3c). The defects extending up to 2 μ m below the machined area are still clearly visible. The two types of defects, the microtwins and

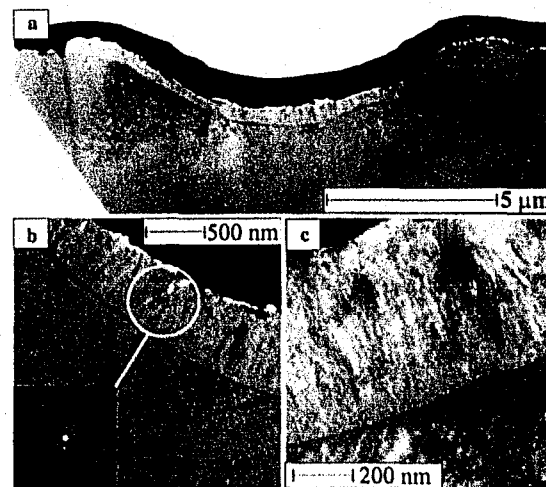


FIGURE 2 TEM cross sectional images of a groove machined in InP with femtosecond pulses (1 μ J, 130 fs). a Low-resolution view b TEM image and diffraction pattern taken near the bottom of the groove c energy-filtered TEM close-up of the resolidified layer

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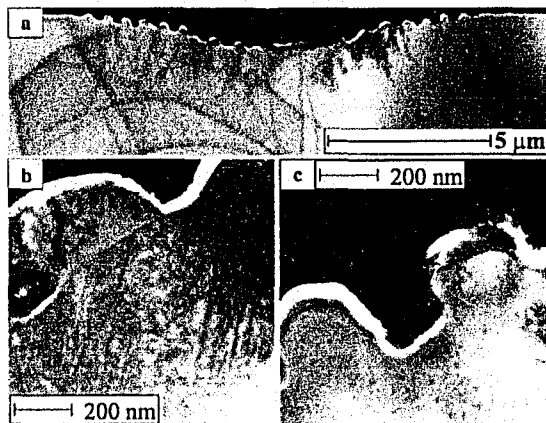


FIGURE 3. TEM cross sectional images of a groove machined in InP with femtosecond pulses (0.35 μJ , 130 fs). a Low-resolution view b energy filtered TEM image taken near the bottom of the groove c energy filtered TEM image taken on the side of the groove

the dislocation networks, observed with 1 μJ pulses (Fig. 2) also are present. However, the distribution of these defects is different and seems to be correlated with the modulation of the LIPSS.

A recent report of strain imaging by polarization resolved photoluminescence [10] revealed significant differences in the nature of strain fields in the vicinity of grooves machined with femtosecond and nanosecond pulses. Most notably the areas which were in tension in femtosecond-machined grooves were in compression in nanosecond-machined grooves. Initial speculations were based on the assumption that the nature of the strain fields is solely caused by difference in the geometry, composition and structure of the resolidified layer. Finite element modeling (FEM) has confirmed that the shape of the strain fields does depend in part on the geometry of the resolidified layer. A fairly good match between simulations and experimental results was obtained for grooves machined with nanosecond pulses, while the agreement was less satisfactory in the femtosecond case. Also the observed sign reversal discussed above was artificially simulated by assuming a negative thermal expansion coefficient. The present TEM results suggest that the defects beneath the grooves as well as the resolidified layer contribute to the residual strain fields observed in vicinity of grooves machined with femtosecond pulses. Including these defects in the model would, therefore, improve

the quality of the simulations. It is also worth pointing out that a closer examination of photoluminescence (PL) images reported in [10] (Fig. 1b) reveals a loss of PL yield in the vicinity of the femtosecond-machined grooves, consistent with the presence of defects which would increase non-radiative recombination channels.

In previous studies, defects resulting from the laser drilling of (100)Si by 50 ns pulses from a copper vapor laser at a fluence $q_0 = 15 \text{ J/cm}^2$ have been reported (see [2], Fig. 8). Two types of defects were found in [2]: 1) dislocations, observed in the heat affected zone and caused by thermally-induced compressive stresses during heating; and 2) cracks, due to the tensile stresses during subsequent cooling. These deformations were, therefore, attributed to thermal rather than mechanical effects. In our case, no defects were observed in grooves machined with nanosecond pulses with a maximum fluence of $q_0 \approx 2 \text{ J/cm}^2$. Furthermore, defects observed below femtosecond-machined grooves extended well beyond the resolidified layer and were even present beneath the grooves machined at low fluences where the amount of resolidified material is minimal. It is, therefore, unlikely that defect formation observed in femtosecond irradiation is due to the same mechanism as discussed in [2].

We expect that the defect formation is partly associated with the high transient pressures reached during the ablation process. In femtosecond irradi-

ation the energy is deposited before any significant hydrodynamic expansion occurs. Furthermore, due to significant nonlinear absorption, the energy is deposited into a smaller volume compared to nanosecond irradiation. Based on simple physical interpretations the effective optical penetration depth of femtosecond pulses is found to be $\sim 30\text{--}60 \text{ nm}$ [12, 13], one order of magnitude smaller than that of low-intensity nanosecond pulses [14]. The net effect is the heating of the material to high temperatures at constant volume, which leads to high thermoelastic pressure buildup [15, 16]. Peak pressures generated by femtosecond pulses at a fluence $\sim 0.5 \text{ J/cm}^2$ have been estimated to be in the range of tens of GPa [17]. These values are significantly higher than the yield strength of InP (around 1.3 GPa) estimated from an indentation study [18]. InP is brittle at room temperature under a conventional uniaxial compression test; however, a confined pressure will suppress brittle fracture and could create twins and dislocations. The equivalent load in indentation experiments necessary to induce the observed defects beneath the grooves (Fig. 3) can be estimated. A simplified version of Johnson's spherical cavity model [19], $P \sim (2/3)\pi\sigma_{ys}c^2$, relates an indentation load (P) with the plastic zone radius (c) and an uniaxial yield strength (σ_{ys}). Using $\sigma_{ys} \sim 1.3 \text{ GPa}$ [18] and $c \sim 3 \mu\text{m}$ (based on our data for the low fluence femtosecond ablation), we obtained an equivalent load of 25 mN. Such a load applied to a spherical indenter induces slip bands in InP on a similar scale. Moreover the load is well above the onset of plasticity for both Vickers [18] and spherical [19] indentation.

Perry et al. [20] considered the pressures associated with high-fluence femtosecond irradiation of fused silica at a wavelength of 1053 nm and a fluence of $\sim 250 \text{ J/cm}^2$. They predicted a pressure drop from 1.2 TPa to a pressure below the yield strength of the material within the first micron. Recently Stach et al. [6] reported TEM studies of single-pulse (800 nm, 300 fs) irradiation of lithium niobate with a fluence of 124 J/cm^2 . They observed a $\approx 100 \text{ nm}$ thick amorphous layer with a highly defective crystalline region extending over $\sim 1 \mu\text{m}$ in length, which appears to be

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qualitatively consistent with the calculations of Perry et al. [20].

In contrast to experiments on ablation of dielectrics discussed above [6], the crystal defects beneath the single pulse ablation craters were not observed in previous plan view TEM investigations of Si [8], InP and GaAs [9]. The fluences in studies reported in [8] and [9] were two orders of magnitude lower than in [6] but comparable to conditions reported in the current paper. The differences which can explain the presence of defects beneath the grooves and absence of similar defects beneath single pulse ablation craters can be considered. First, the single pulse TEM analysis was performed in plan view, that is, craters were viewed from above. In plan view the analysis of microstructure is complicated by the fact that the ablation craters are located on top of an unaffected substrate. The diffraction patterns therefore contain contributions from the resolidified layer and the underlying substrate. Defects extending deeper into the substrate would also be impossible to observe since the process of sample preparation involves back thinning of the sample to a thickness of the order of 100 nanometers. The advantage of cross sectional TEM stems from the fact that the resolidified layer can be viewed directly without any background. Secondly, in the process of cutting grooves we estimate that ~ 15 pulses are incident on the surface over an area equivalent to our beam diameter. After the first pulse, subsequent pulses encounter material with modified, chemical, structural and optical properties [12, 21, 22] leading to cumulative effects, usually explained via incubation effects [23]. In the original work Jee et al. [23] related the incubation process to accumulation of energy via plastic stress-

strain of the crystalline metals. In ablation of InP, Bonse et al. [12] also suggested the possibility of energy storage in the form of crystallographic changes, such as amorphization/recrystallization and chemical changes following single pulse irradiation. Material modifications in conjunction with thermal cycling and repetitive transient shock during multiple pulse irradiation are expected to play a key role in the formation of the microstructures and defects observed in the current work.

In summary, we have presented a detailed analysis of the microstructure of grooves machined in InP by 130 fs and 8 ns laser pulses. Understanding the mechanisms of defect formation is important if femtosecond laser micro-machining is to be used in practical applications, such as the repair of optoelectronic devices [24]. The extended defects observed in femtosecond (and not nanosecond) machining limit the precision of the technique. Future studies on compound semiconductors exploring further the dependence of defect formation on laser pulse length, pulse fluence, and scan speed (number of pulses) would be of definite interest.

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REFERENCES

- 1 See e.g., B.N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, A. Tünnermann: *Appl. Phys. A* **63**, 109 (1996); X. Liu, D. Du, G. Mourou: *IEEE J. Quantum Electron.* **QE-33**, 1706 (1997); L. Shah, J. Tawney, M. Richardson, K. Richardson: *Appl. Surf. Sci.* **183**, 151 (2001); G. Kamlage, T. Bauer, A. Ostendorf, B.N. Chichkov: *Appl. Phys. A* **77**, 307 (2003).
- 2 A. Luft, U. Franz, A. Emsermann, J. Kaspar: *Appl. Phys. A* **63**, 93 (1996).
- 3 R. Le Harzic, N. Huot, E. Audouard, C. Jonin, P. Laporte, S. Valette, A. Fraczkiewicz, R. Fortunier: *Appl. Phys. Lett.* **80**, 3886 (2002).
- 4 H. Dömer, O. Bostanjoglo: *J. Appl. Phys.* **91**, 5462 (2002).
- 5 T. Gorelik, M. Will, S. Nolte, A. Tünnermann, U. Glatzel: *Appl. Phys. A* **76**, 309 (2003).
- 6 E.A. Stach, V. Radmilovic, D. Deshpande, A. Malshe, D. Alexander, D. Doerr: *Appl. Phys. Lett.* **83**, 4420 (2003).
- 7 G.K. Giust, T.W. Sigmon: *Appl. Phys. Lett.* **70**, 767 (1997).
- 8 A. Borowiec, M. MacKenzie, G.C. Weatherly, H.K. Haugen: *Appl. Phys. A* **76**, 201 (2003).
- 9 A. Borowiec, M. MacKenzie, G.C. Weatherly, H.K. Haugen: *Appl. Phys. A* **77**, 411 (2003).
- 10 A. Borowiec, D.M. Bruce, D.T. Cassidy, H.K. Haugen: *Appl. Phys. Lett.* **83**, 225 (2003).
- 11 M.W. Phaneuf: *Micron* **30**, 277 (1999).
- 12 J. Bonse, J.M. Wrobel, J. Krüger, W. Kautek: *Appl. Phys. A* **72**, 89 (2001).
- 13 A. Borowiec, H.K. Haugen: *Appl. Phys. A* **79**, 521 (2004).
- 14 E.D. Palik: *Handbook of Optical Constants of Solids* (Academic Press, San Diego, California 1985), p. 511.
- 15 D. Perez, L.J. Lewis: *Phys. Rev. B* **67**, 184102 (2003).
- 16 C. Schafer, H.M. Urbassek, L.V. Zhigilev: *Phys. Rev. B* **66**, 115404 (2002).
- 17 K. Sokolowski-Tinten, J. Bialkowski, A. Cavalleri, D. von der Linde, A. Oparin, J. Meyer-ter-Vehn, S.I. Anisimov: *Phys. Rev. Lett.* **81**, 224 (1998).
- 18 E. Le Bourhis, G. Patriarche: *Phil. Mag.* **A82**, 1953 (2002).
- 19 D. Kramer, H. Huang, M. Kriese, J. Robach, J. Nelson, A. Wright, D. Bahr, W.W. Gerberich: *Acta Mater.* **47**, 333 (1999).
- 20 M.D. Perry, B.C. Stuart, P.S. Banks, M.D. Feit, V. Yanovsky, A.M. Rubenchik: *J. Appl. Phys.* **85**, 6803 (1999).
- 21 J. Bonse, J.M. Wrobel, K.W. Brzezinka, N. Esser, W. Kautek: *Appl. Surf. Sci.* **202**, 272 (2002).
- 22 J. Bonse, M. Lenzner, J. Krüger: *Modification and ablation of semiconductors by femtosecond laser pulses* In: *Recent Res. Devel. Applied Phys.* **5** (part II) (Trivandrum, India, Transworld Research 2002), pp. 437–461.
- 23 Y. Jee, M.F. Becker, R.M. Walser: *J. Opt. Soc. Am. B* **5**, 648 (1988).
- 24 E. Dupont, X. Zhu, S. Chiu, S. Moisa, M. Buchanan, M. Gao, H.C. Liu, P.B. Corkum: *Semicond. Sci. Technol.* **15**, L15 (2000).

The work presented provides a new insight and new information about the microstructure and defect formation in the vicinity of laser machined grooves. Perhaps the most noteworthy and unexpected result was the observation of crystal defects beneath the grooves machined with femtosecond pulses. These findings support the conclusion that the femtosecond pulses do not necessary guarantee defect free machining. In this study, only two extreme cases of femtosecond and nanosecond pulse irradiation were investigated. A natural extension of the work would include investigation of grooves machined with pulse duration between ≈ 8 ns and ≈ 130 fs. With the pulse energy and all other beam parameters held constant, decreasing the pulse duration leads to an increasing laser intensity incident on the sample. As the intensity increases the nonlinear effects start to play an important role and lead to an increase of the effective absorption coefficient and hence deposition of the energy within a smaller volume. Higher heating rates caused by decreasing pulse duration in conjunction with a smaller volume lead to increasing stress buildup. It is reasonable to expect, that at some critical pulse duration, the thermoelastic stress would be released by formation of crystal defects, observed here in the limit of femtosecond machining. Since TEM analysis is difficult, sets of grooves would first be examined by DOP imaging. Examination of both the spatially resolved PL and DOP images could indicate at which pulse duration the defects start to form, and identify samples most suitable for TEM analysis. Combined TEM, DOP, micro-Raman analysis and FEM modeling will provide a very complete assessment of the final state of the material after laser micromachining of grooves and other features.

Chapter 6

Summary and Outlook

6.1 Summary

The work presented in this thesis is most conveniently divided into two sets of investigations: the single and multiple pulse ablation of stationary targets described in Chapter 4 and micromachining and analysis of grooves cut in InP described in Chapter 5.

The single and multiple pulse ablation experiments were performed with femtosecond pulses, 60 – 150 fs in duration, centered around wavelengths of 400, 800, 660, 800, 1300 and 2100 nm. The post mortem analysis was performed with a variety of microscopy techniques including SEM, OM, AFM and TEM. The ablation thresholds at various wavelengths were determined based on the discontinuity in the maximum crater depth and the discontinuity in the crater volume vs. fluence measurements. The formation of coherent surface structuring after multiple pulse irradiation of stationary samples was investigated on InP and other III-V and IV semiconductors and sapphire. Conditions required for formation of the ripple structures were identified but the exact mechanism of formation of these patterns is still an open question.

The experiments involving micromachining of grooves in InP were performed with ≈ 130 and ≈ 8 ns pulses, at wavelengths centered around 800 nm. The dependence of the ablation rate of femtosecond pulses on various machining parameters was measured via SEM. The DOP measurements were performed on selected grooves to study the photoluminescence efficiency and the residual strain resulting from femtosecond and nanosecond laser micromachining. Significant differences in the geometry of the strain patterns were observed in grooves machined in the two temporal domains. Detailed cross-sectional TEM analysis of the microstructure was performed for grooves micromachined in femtosecond and nanosecond temporal domains. Substantial densities of defects were observed beneath the grooves machined with femtosecond pulses.

6.2 Outlook

Suggestions for further studies specific to each set of experiments were included at the end of each section in Chapters 4 and 5. In addition to extending the experiments

to different materials and a wider range of laser parameters, several additional possibilities for further research can be considered.

One interesting perspective for ultrafast ablation research involves the use of temporally shaped pulses. Most femtosecond lasers produce pulses with a Gaussian temporal profile. It is often assumed that ablation with the shortest pulses leads to the best machining results. This assumption is true for some materials, such as sapphire and fused silica [99]. In cases of brittle materials, such as CaF_2 it is beneficial to deliver the energy in a sequence of several weaker femtosecond pulses separated by a few hundred femtoseconds [100]. The use of temporally shaped femtosecond pulses exploits the dynamics of energy deposition and dissipation within the interaction volume. Modulated energy input leads to controlled heating and softening of the lattice, and reduction of stress buildup during the ablation process. The first results of ablation of silicon with temporally shaped pulses were recently reported [101, 102]. Temporal synthesis of arbitrary pulse shapes is the most flexible technique but it requires the use of sophisticated equipment [103]. An alternative approach involves the use of burst machining [104,105]. In burst machining, the energy is deposited by a train of several hundred femtosecond or picosecond pulses separated by few nanoseconds. In the context of the work presented, the use of temporal pulse shaping would be particularly well suited in the study of defect formation beneath grooves machined with femtosecond pulses. More specifically, determining the optimum pulse duration, pulse separation and the energy of individual pulses that minimize the residual strain and defect densities resulting from femtosecond laser machining would be of interest.

Spatially and polarization resolved photoluminescence imaging (DOP) proved to be very valuable in analysis of strain fields resulting from laser micromachining of InP. However, the current DOP imaging setup is limited to analysis of light emitting materials, such as direct band-gap III-V semiconductors. Imaging of direct band-gap dielectrics is possible but requires a deep UV pump laser. However, a femtosecond oscillator could replace the UV laser. The principle of DOP imaging utilizing multi-photon pumping was already demonstrated in our laboratory on GaP pumped by a femtosecond oscillator at central wavelength of 800 nm. This configuration would provide a convenient method of extending the DOP imaging to wide band-gap semiconductors and dielectrics. An extension of DOP imaging to indirect band-gap semiconductors and metals would also be of great interest but requires an alternative approach. One possibility involves the use of reflection geometry to study the changes of the polarization state of light at the reflection from the interface [106]. The development of new analysis tools, such as multi-photon or reflection mode DOP imaging is another interesting perspective for further research.

All results presented in this thesis relied on post mortem analysis of lateral and vertical dimensions of the ablation craters. The ability to probe the ablation dynamics would be of great interest. The recently reported technique of time-resolved interferometric microscopy [107] is capable of temporally resolving the lateral and vertical evolution of surfaces excited by femtosecond pulses. The authors in Ref. 107 reported a temporal and spatial resolution of 100 fs and 1 μm respectively, and an ability of detecting surface deformation of 1 nm and 1 percent change in surface reflectivity. The study of GaAs excited by femtosecond pulses was also demonstrated. Application of

a time resolved technique would be an excellent prequel to the post mortem analysis studies presented.

6.3 Concluding Remarks

The experiments presented in this thesis were largely exploratory in nature and covered several different aspects of laser ablation and micromachining of InP. The work serves as an excellent foundation for future research in the field. Constant refinement of experimental techniques, development of new analytical tools and on-going theoretical work will without a doubt lead to more complete understanding of the ablation process. Further advances in the ultrafast laser technology, and development of more powerful and cheaper laser systems will likely lead to more widespread use of femtosecond laser systems in many technological applications.

Appendix A

This appendix contains two previously published papers, which summarize work completed during my Masters Degree.

A.1. X-Ray Emission From Femtosecond Laser Micromachining

This paper presents results of spectral characterization and absolute dose measurements of x-ray emission resulting from irradiation of various metal and semiconductor targets, under conditions potentially encountered during laser micromachining.

Dr. Jan Thøgersen was the principal researcher and author of the manuscript. This work was started during my first year of graduate studies and I provided assistance with all experimental aspects of the work presented.

X-ray emission from femtosecond laser micromachining

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Abstract. We characterize the spectral properties of X-rays generated from selected metal and semiconductor targets when 120-fs laser pulses are focused to intensities of $\sim 10^{14}$ – 3×10^{15} W/cm² during laser micromachining in air. High fluxes of multi-keV-energy X-rays could be obtained with 280-pJ pulses at a 1 kHz repetition rate. The yield and spectral composition of the X-rays are found to depend sensitively on the processing conditions, and thus the X-ray emission is expected to be a novel indicator of optimal laser machining.

PACS: 42.62Cf; 61.80Ba; 78.70Fn

Femtosecond lasers are becoming important tools in materials microprocessing [1–4]. Ultrashort laser pulses lead to a qualitatively different interaction with solids, resulting in higher resolution cuts with less damage to the surrounding material. The lasers deployed in femtosecond laser machining commonly have pulse energies ranging from 0.1 pJ to 1 mJ and repetition rates in the 1–250 kHz regime. Tight focusing leads to peak laser intensities $\sim 10^{12}$ – 10^{17} W/cm² and the production of X-rays. Despite the fact that X-rays are known to be generated at these laser intensities [5–12], attention has not been given to X-ray emission resulting from femtosecond laser micromachining. In part, this is due to the fact that laser-produced X-ray research has normally been conducted under vacuum conditions with high-pulse-energy, low-repetition-rate systems. Studies in air have generally been lacking and the important connection with materials processing has not been established. This preliminary investigation characterizes the X-rays generated with intensities $\sim 10^{14}$ – 3×10^{15} W/cm² and briefly discusses potential applications for laser machining.

1 Experimental

A regeneratively amplified Ti:sapphire laser produced 120-fs pulses at a repetition rate of 1 kHz and with a maximum pulse energy of 0.3 mJ. Figure 1 shows two typical experimental setups. In Fig. 1a, a 50-mm-focal-length plano-convex lens was employed to focus the laser beam at 45°, with the X-rays being detected in air perpendicular to the sample surface. In the configuration of Fig. 1b, either a 25-mm-focal-length graded index lens or a 10× microscope objective was employed to focus the laser beam perpendicularly to the target surface, with the X-rays detected at $\approx 45^\circ$. The perturbation by air in our work did not seem to significantly affect the generation of multi-keV X-rays. The target was controlled on an xyz-translation stage with a maximum speed of 200 μ m/s. X-ray spectra were measured using two different detectors (Si:Li and Ge). Since laser-produced X-rays are emitted in picosecond bursts which are orders of magnitude shorter than the detector response time [8], in spectroscopic measurements pulsed X-ray emission can lead to pile-up artifacts. Spectral distortion was minimized by inserting an aper-

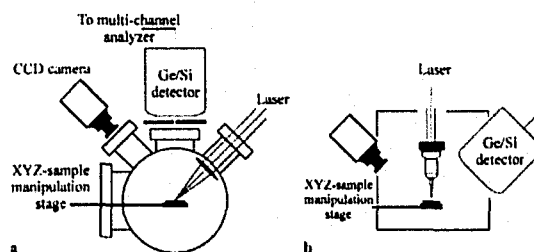


Fig. 1a,b. Schematic of our typical experimental setups: a A plano-convex lens was used to focus laser pulses at an angle of 45° on target in a stainless steel chamber. A 1-mm-thick steel plate with a 1.5-mm-diameter aperture was positioned in front of the Si:Li or Ge solid-state detector used for X-ray spectroscopy at a 13-cm distance. b A graded index lens or microscope objective focuses the laser perpendicularly to the surface, with X-ray monitoring at 45° and a detector distance of 5 cm

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ture (Fig. 1a), ensuring an average count rate less than one event per 10 laser pulses. In separate measurements, the X-ray dose-rate was measured by a thin-windowed ionization monitor (Bicron RSO-5) with a low-energy gradual cut-off around 8 keV.

2 Results and discussion

X-ray spectra taken perpendicular to the target (Fig. 1a) were observed from several samples including Al, Ti, Cr, Fe, Cu, Zn, Ge, Nb, Mo and W. For laser pulse energies of 240–280 μJ , K-radiation was obtained for all elements with K-line energies less than 11 keV, corresponding to elements with atomic numbers $Z < 32$, whereas for elements with $Z > 32$ only a continuum was measured. In separate measurements using a 25-mm-focal-length graded index lens (Fig. 1b), the Cu spectrum was recorded as a function of laser pulse energy. The Cu spectrum of Fig. 2a consists almost exclusively of K-line radiation (8.0 keV K_α and 8.9 keV K_β), whereas Fig. 2b illustrates the rapid drop in the ratio between the line and continuum emission with decreasing laser intensity. Systematic investigations of the relationship between line and continuum emission employing Cu, Fe and Ti targets demonstrated that K-line radiation can be observed when the laser intensity is sufficiently high to efficiently create K-shell vacancies. A series of additional measurements with a (10 $\times$) microscope objective revealed the production of continuum radiation up to 4 keV at a pulse energy as low as 0.7 μJ . These focal conditions are not diffraction-limited and could be substantially improved in future work.

The X-ray yield emitted from the copper target was also measured by the Bicron RSO-5 monitor positioned 13 cm from the laser focus. The target was translated at 150 $\mu\text{m/s}$, meaning that $\sim 1\%$ of the exposed target was replaced by pristine copper for every laser pulse. We were able to achieve

(corrected) dose rates for X-rays with energies within the sensitivity range of the monitor as high as $\sim 10 \text{ mSv/h}$ ($\sim 1 \text{ rem/h}$). Assuming isotropic emission and the factory-specified detector efficiency, we estimate that the total X-ray yield into 2π steradians within the monitor's energy range was $\sim 10^8 \text{ s}^{-1}$ (10^5 per laser pulse).

The high multi-keV X-ray yields demonstrate that hard radiation signals from laser machining can be monitored in air. We observed the X-ray yield to increase as $I^{2.8 \pm 0.3}$ for the intensity range $1\text{--}3 \times 10^{15} \text{ W/cm}^2$, indicating that the production mechanism operates in a sensitive nonlinear regime. Our yields also increased strongly with increased target speed; hence much higher X-ray fields could be produced if the translation speed ensured a pristine sample for each pulse. In contrast, little or no radiation was observed from stationary targets since the target material at the high-intensity beam waist is quickly ablated. When machining holes, shadowing effects are expected for observation angles outside a cone perpendicular to the target; thus selection of the X-ray monitoring angle might serve to monitor machining depths in future micromachining systems¹. Measurements of the line-versus-continuum radiation provides information on the plasma temperature, and therefore with samples of nonuniform elemental composition, measuring characteristic X-rays could be employed to reduce collateral damage. Furthermore, the combined intensity and spectral selectivities suggest prospects for sub-micron control in the selective ablation and marking of solid surfaces.

Finally, we note that quantitative X-ray dose-rate values have not, to our knowledge, been reported for the intensity regime associated with ultrafast laser materials processing. The high dose rates ($\sim 10 \text{ mSv/h}$ at 13 cm distance) observed in this work should be taken into account in terms of radiation shielding of the apparatus [13]. X-rays with energy less than $\approx 5 \text{ keV}$ are strongly attenuated in air, and thus the main shielding effort for our system concerns the 5–20 keV range. Radiation in this energy regime has been eliminated by mm-thick sheets of steel [13].

3 Conclusion

The high efficiency of multi-keV X-ray production from micromachining processes with ultrashort-pulse kHz lasers suggests important applications. Issues which will define precisely the ultimate deployment of the X-rays in monitoring ultrafast materials processing, such as the polarization and angular dependencies, the spatial extent of X-ray emission relative to the laser plasma volume, the intensity dependence over a wide dynamic range, and the role of ambient air, warrant further detailed investigations.

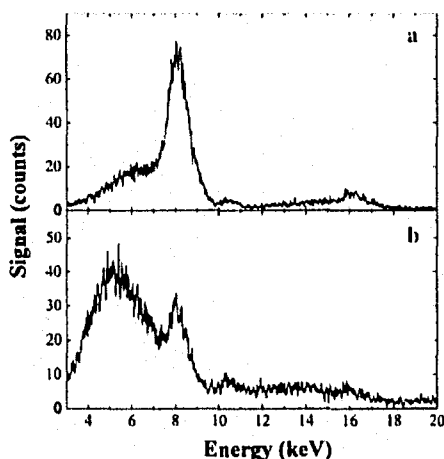


Fig. 2a,b. X-ray spectra measured in air from a copper target for two laser pulse energies: 8.4 μJ (a), and 2.8 μJ (b). The relative scales of the two spectra are not normalized. Low-level pileup effects are evident at energies greater than 10 keV (see text)

¹ For an X-ray energy range of 5–10 keV, the attenuation coefficients for several metals and semiconductors provide extinction lengths on the micron length scale [13].

² The recommendations of the International Commission on Radiological Protection (ICRP) indicate via ICRP-60 [13] an annual occupational exposure limit of 20 mSv, an equivalent annual dose limit of 150 mSv to the lens of the eye, and 500 mSv for skin, hands and feet of workers. For continuous or frequent exposure, the recommended annual limits for the public are 1 mSv, an equivalent annual dose limit of 15 mSv for the lens of the eye, and 50 mSv to skin, hands and feet. These limits are intended as a regulatory instrument; doses should be kept as low as reasonably possible, and should normally be far below these figures.

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References

1. X. Liu, D. Du, G. Mourou: *IEEE J. Quantum Electron.* **QE-33**, 1706 (1997)
2. D. Ashkenasi, H. Varel, A. Rosenfeld, S. Henz, J. Herrmann, E.E.B. Campbell: *Appl. Phys. Lett.* **72**, 1442 (1998)
3. A. Cavalleri, K. Sokolowski-Tinten, M. Schreiner, D. von der Linde: *J. Appl. Phys.* **85**, 3301 (1999)
4. X. Zhu, D.M. Villeneuve, A.Y. Naumov, S. Nikumb, P.B. Corkum: *Appl. Surf. Sci.* **152**, 138 (1999)
5. I.C. Tureci, J.B. Dance: *X-rays From Laser Plasmas: Generation and Applications* (Wiley, New York 1998)
6. C. Rose-Petruck, R. Jimenez, T. Guo, A. Cavalleri, C.W. Siders, F. Ráksi, J.A. Squier, B.C. Walker, K.R. Wilson, C.P.J. Barty: *Nature* **398**, 310 (1999)
7. C. Tilmann, I. Mercer, S. Svanberg, K. Hertlin: *J. Opt. Soc. Am. B* **13**, 209 (1996)
8. See, for example, M.M. Murnane, H.C. Kapteyn, S.P. Gordon, R.W. Falcone: *Appl. Phys. B* **58**, 261 (1994); F. Ráksi, K. Wilson, Z. Jiang, A. Ikhlef, C.Y. Côté, J.C. Kieffer: *J. Chem. Phys.* **104**, 6066 (1996)
9. A. Saemann, K. Eidmann: *Appl. Phys. Lett.* **73**, 1334 (1998)
10. M. Schnürer, M.P. Kalashnikov, P.V. Nickles, T. Schlegel, W. Sandner, N. Demchenko, R. Nolte, P. Ambrosi: *Phys. Plasmas* **2**, 3106 (1995)
11. J.D. Kmetec, C.L. Gordon III, J.J. Macklin, B.F. Lemoff, G.S. Brown, S.E. Harris: *Phys. Rev. Lett.* **68**, 1527 (1992)
12. H. Hamster, A. Sullivan, S. Gordon, W. White, R.W. Falcone: *Phys. Rev. Lett.* **71**, 2725 (1993)
13. J.E. Turner: *Atoms, Radiation, and Radiation Protection*, 2nd edn. (Wiley, New York 1995); A. Holmes-Siedle, L. Adams: *Handbook of Radiation Effects* (Oxford University Press, 1993)

A.2. Scanning and Transmission Electron Microscopy Studies of Single Femtosecond-Laser Pulse Ablation of Silicon

This paper presents plan view TEM studies of single pulse ablation craters on Si. At the time of publication it was the first report of detailed TEM investigation of single pulse ablation craters resulting from femtosecond laser irradiation of Si.

I was primarily responsible for the laser ablation work, and writing of parts of the manuscript. Large portion of this manuscript, especially the discussion section was written by Dr. Harold Haugen. Andy Duft prepared the plan view TEM sample and Dr. Maureen MacKenzie and Dr. George Weatherly carried out all of the TEM work.

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Applied Physics A
Materials Science & Processing

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Transmission and scanning electron microscopy studies of single femtosecond-laser-pulse ablation of silicon

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ABSTRACT The final state of the material resulting from laser irradiation of silicon using 130 fs pulses at 790 nm was studied using a number of techniques including scanning and transmission electron microscopies, as well as atomic force microscopy. Structural details and the level of damage to the nearby solid following irradiation were characterized and are discussed in the context of recent dynamical studies.

PACS 61.80.Ba; 64.60.-i; 79.20.Ds

1 Introduction

Laser processing of semiconductors has been an area of intense fundamental and applied research for many years due to the technological importance of semiconductors (see, e.g. [1–3]). A large amount of information is available on this topic, however, much of the work covers cw and nanosecond laser processing. In part stimulated by applications in the micromachining and micromodification of a wide range of materials [4–11], the study of heating, melting and ablation of semiconductors has more recently been extended with an emphasis on ultrafast pulse irradiation as well as temporal analysis of the target response [12–29]. The dynamics of single-laser-pulse interaction with semiconductor surfaces has been investigated by a number of techniques including optical pump-probe [12–15], time-of-flight mass spectroscopy [16], time-resolved microscopy [17, 18], and temporally-resolved X-ray diffraction [19–22]. A number of theoretical models have also been proposed to model ultrafast heating and ablation processes [23–26].

Although extensive recent studies have revealed remarkable aspects of the ablation process, very little work has been

conducted aimed at the microscopic details of the final state of the material [28–31]. Also, despite the fact that femtosecond laser micromachining is often considered “damage-free”, in contrast to processing with much longer pulses, studies which explore the limits of this assumption are essentially lacking. In this first study, we have concentrated on single-shot laser experiments on Si (100) utilizing pulse energies and tight focussing conditions, which lead to target modification features on the few-micron scale. In particular, we have examined the effects of the laser irradiation process on the structure and composition of the Si target. Analytical tools used to study the properties were scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and electron energy-loss spectroscopy (EELS). Most importantly, extensive TEM studies provide unique information on the nature of re-solidified target material and the extent and type of damage to the solid. Our TEM investigations included searching for whole or partial dislocations, and/or twins, as have been observed at hardness indentations in silicon where pressures comparable to those reported for single-shot laser experiments are encountered.

2 Experimental

Laser pulses of 130 fs duration with a wavelength of approximately 790 nm were obtained from a (nominal) 1 kHz repetition rate amplified Ti:sapphire laser. Typically, the laser beam was focussed on the sample by a 10× microscope objective (Newport M-10x), which has an entrance aperture of 7.5 mm. The spot size ($2\omega_0$) of 6.7 μm at the focus was measured by a scanning knife-edge technique. With the pulse repetition rate reduced to 10 Hz, a fast mechanical shutter, synchronized with the laser, was used to control the number of pulses delivered to the sample. In a few selected studies using a separate laser system and focussing set-up, 60-fs laser pulses were utilized for irradiations in air. The laser machining process was monitored on-line with a confocal imaging system and a CCD camera. Although a few irradiations were performed in air, for most detailed TEM studies Si (100) samples were placed inside a small vacuum chamber mounted on a computer controlled xyz translation stage and machined under rough vacuum (~0.1 mbar). The laser beam was delivered through a thin, uncoated sapphire window

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(200 μm thick) cut perpendicular to the c -axis with pulse energies ranging from 1.9 μJ to 10 nJ. The energy of the laser was adjusted with a set of thin (1 mm thick) reflective neutral density filters in steps of 0.1 OD ($\text{OD} = \log(I_0/I)$), where I_0 is the input intensity, and I the output intensity). These filters were cascaded to obtain the desired pulse energy. The uncertainty in the laser fluence was approximately 50% due to the combined uncertainties in the fundamental laser spot size, target positioning and the pulse energy. This aspect is particularly challenging in the present work due to the very small focal spots that were utilized.

Changes in surface morphology and size of the laser-induced features were first characterized by means of scanning electron microscopy. The depth and crater profiles were measured with atomic force microscopy in the contact mode. Plan-view specimens suitable for TEM studies were prepared using standard preparation techniques of mechanical back-thinning followed by argon-ion-beam milling until electron transparency was achieved. The sample preparation method involved the use of an epoxy cement that required heating of the sample to a maximum temperature of 200 °C. Crystal structure and composition in the vicinity of the ablation sites were investigated using a variety of TEM techniques. Standard bright- and dark-field imaging were used to study the shape and size of the craters and the structure of the re-solidified material. These techniques incorporated an aperture in the back focal plane of the objective lens to select the electrons used to form either a bright-field or dark-field image. A Philips CM12 conventional transmission electron microscope, operated at 120 kV, was employed for this purpose. Standard selected-area diffraction and convergent-beam electron diffraction were utilized to determine the crystallographic structures of the regions investigated. Chemical analyses were performed on a field-emission-gun JEOL 2010F scanning transmission electron microscope operated at 200 kV. The JEOL 2010F was equipped with an EDX-UTW Link ISIS system for analytical X-ray spectroscopy and a Gatan 666 electron energy-loss spectrometer. The energy-loss spectrum was used to measure the depth of the near-threshold laser-induced features using a mean free path of 100 nm for silicon.

3 Results

Figure 1 shows a montage of SEM images of single-shot craters produced by pulses with energies ranging from 35 nJ to 1.9 μJ . Under our experimental conditions, the damage threshold of Si – as defined by an observable surface change detected via high-resolution SEM – was found to correspond to a laser-pulse energy of approximately 25 nJ with a corresponding energy fluence of approximately 150 mJ/cm². As discussed further in Sect. 4 below, within the associated uncertainties, the observed threshold is consistent with that reported in the literature. For example, Downer and Shank quote a damage threshold of 100 mJ/cm² for 100-fs, 620-nm pulses [14] while Cavalleri et al. quote a melting threshold for Si of 150 mJ/cm² for 100–120 fs pulses of 620 nm wavelength [16]. While the damage threshold corresponds to an observable change in the SEM analysis, the ablation threshold will be defined in terms of the removal of

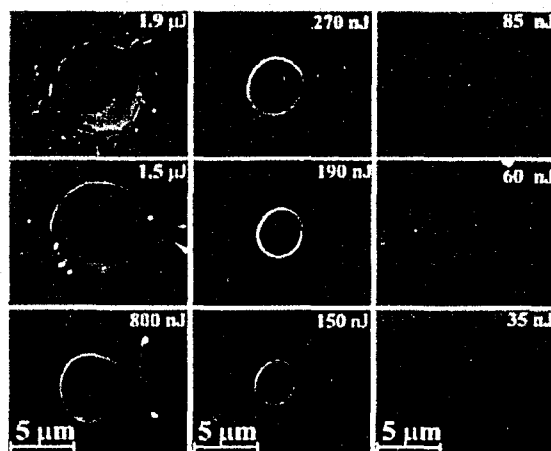


FIGURE 1 SEM images of single-shot ablation craters produced by 130-fs pulses with energies ranging from 35 nJ to 1.9 μJ

a significant amount of material. This is often measured via back-extrapolation of the squared diameter of the observed craters as a function of laser fluence, as discussed further below.

Although no abrupt changes in the surface morphology were observed with increasing pulse energy, it is convenient to discuss three characteristic fluence regions, which follow the interpretation of the dynamical studies of Cavalleri et al. [16]. In our work, these regions can be qualitatively identified based on the observed surface morphology and debris patterns. The first interval of laser-pulse energies is the near damage threshold and corresponds approximately to the range 25 nJ < E < 50 nJ. In the second interval, corresponding to pulse energies in the range 50 nJ < E < 300 nJ, a very distinct circular rim forms around the craters. A third pulse-energy bracket, observed with pulse energies of E > 300 nJ, corresponds to a more violent expulsion of material from the crater. This resulted in very asymmetrically re-solidified material and in general the deposition of solidified Si droplets both inside and outside of the crater region. Figure 2 shows AFM profiles of the laser-induced features for pulse energies ranging from 60 nJ to 1.9 μJ . The volume below the original plane of the surface was found to scale approximately linearly with the laser-pulse energy. As discussed further below, a more precise determination of the rim volumes will be required in order to specify an accurate value for the ablation threshold within the context of the dynamical models.

For laser-pulse energies > 25 nJ, very small features were observed, indicating that the damage threshold had been exceeded. The surface morphology as observed in the SEM was indicative of melting followed by epitaxial re-solidification with minimal loss of material. At the material damage threshold, features as small as 500 nm could be obtained under optimal focussing conditions. With an increase of the pulse energy, the size of the damaged area increased up to almost 2 μm . In this case, the size of the affected area was always much smaller than the laser spot size ($2\omega_0 = 6.7 \mu\text{m}$), where only the intensity over the central part of the beam exceeded the damage threshold. This sensitivity also means that the

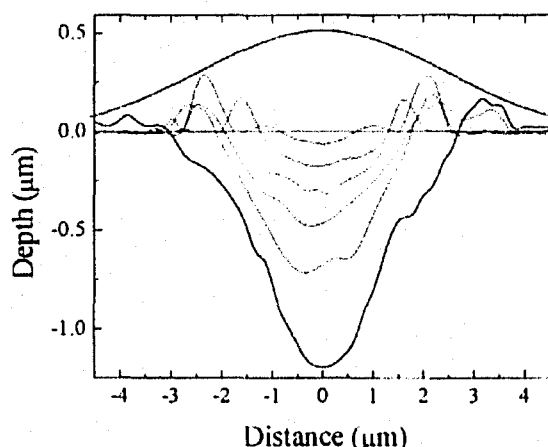


FIGURE 2 AFM profiles of craters for various pulse energies in order of increasing depth: 60 nJ, 145 nJ, 275 nJ, 500 nJ, 840 nJ and 1.9 μ J. The shape of an input Gaussian laser beam, with a transverse size corresponding to our focal spot determination, is illustrated at the top

optical alignment of the focusing objective is crucial. Even a small degree of defocus leads to a rapid decrease in the beam intensity on the surface, which can either cause fluctuations in the diameter of the craters or even reduce the fluence such that it is below the damage threshold of the material.

There are several challenges in the TEM analysis of the laser-induced structures. In the case of features produced by energies just above the damage threshold, the greatest challenge is isolating information from the affected material. Single-shot craters near the damage threshold are only several nanometers deep, while the thickness of the underlying thinned substrate can be several tens of nanometers. In such cases, information from the relevant region can be masked by information from the unaffected substrate material and the sensitivity of analysis may not be sufficiently high to detect compositional or crystallographic changes in the affected material. Figure 3 shows TEM images of features in the near-threshold regime, taken from the first fluence bracket. The bright-field image in Fig. 3a was formed using undiffracted electrons and shows a feature of about 2 μ m in lateral extent. Also shown in Fig. 3a are selected-area diffraction patterns taken from the modified region and from the nearby unaffected silicon. Examination of both diffraction patterns reveals a weak ring pattern superimposed on the stronger single-crystal (100) Si spot pattern. We interpret this ring pattern to result from surface oxidation caused by the ion beam milling and that it is not a result of the laser interaction. Such an effect will always be present on the material surface but will be masked in thicker regions by the bulk material. It is particularly pronounced in thinner regions of material, regardless of whether or not it has been laser-irradiated. The quantities of oxygen detected in irradiated regions were on a similar level to those detected in thin regions of unaffected substrate, consistent with the oxygen being a surface effect resulting from the ion milling process. A second feature from this regime is shown in the dark-field image of Fig. 3b, formed using a diffracted beam of electrons. This feature shows a series of

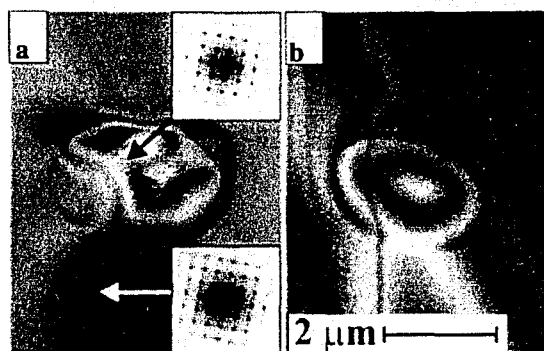


FIGURE 3 TEM images and diffraction patterns taken from irradiations close to the damage threshold: a a bright-field image with diffraction patterns from indicated regions; and b a dark-field image. Bright- and dark-field images are utilized in order to obtain optimal contrast under various circumstances. Note that in this case the irradiations were not performed under the tightest focusing conditions.

near-circular fringes which can be used to deduce that this is a shallow, bowl-shaped feature left at the surface as a result of laser irradiation at this fluence. EELS was used to verify that even in this regime there was some removal of material resulting in the formation of features with depths of approximately 10 nm at their centres. TEM analysis of the areas immediately outside of the craters showed no evidence of structural or surface damage.

When the laser-pulse energy was increased by approximately a factor of two above the material damage threshold, roughly corresponding to an energy fluence of 300 mJ/cm², more significant material displacement was observed. For the range of pulse energies of 50 nJ to 300 nJ, the craters were typically symmetric, and well defined with pronounced rims, with no significant debris beyond the crater area for vacuum irradiation conditions. The laser-material modification process in this regime was essentially 100% reproducible and identical craters could be processed across the entire length of the sample. Craters for this laser fluence bracket exhibited a characteristic rim $\approx$ 50–150 nm high on the outer edge. They were typically between 3 and 5 μ m in diameter and $\approx$ 100–400 nm deep.

Figure 4a shows a TEM image of a crater produced by irradiation in air using a 60 fs-pulse with an energy of 160 nJ. A convergent-beam electron diffraction pattern from the centre of this crater is shown in the inset. The material in the crater can be seen to be of a quality comparable to virgin crystal, i.e. there are no extended or point defects present. (The presence of such defects would degrade the quality of the diffraction pattern, particularly in the high-angle regime of the higher-order Laue zone, which appears as a circle in this pattern.) The rim, which is 300 nm wide, has solidified as single crystal material containing many defects. Figure 4b shows a blow-up of the rim. The small-scale debris that is visible is typical of irradiations in air. Rims with polycrystalline grains of the order of 20 nm were also obtained in this regime. In addition, some amorphous-like layers were found on some of the rims produced, although many of these were very thin and in some cases had traces of crystallinity. The exact nature of the rims that are formed is expected to depend primarily on the rate of

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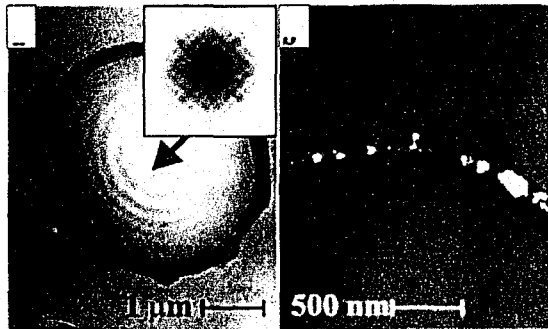


FIGURE 4 TEM images taken from: a a crater formed by a 160-nJ, 60-fs pulse irradiation in air, with the diffraction pattern shown for the inner region; and b a magnified view of the rim

cooling of the Si in the rim during the solidification process, which will in turn depend on the deposition and dissipation of energy in the material.

A different crater morphology was observed when the pulse energy was increased beyond approximately 300 nJ. With this further increase in the laser-pulse energy, the surface morphology continued to degrade, and especially above 500 nJ, droplets of Si approximately 200 nm in diameter could be seen beyond the outer rims of the craters. In craters ablated by 1.9 μJ -pulses, large debris patterns of frozen semiconductor material were found far beyond the rims. In that case, the volume of displaced semiconductor was measured to be $9 \mu\text{m}^3$, and $3 \mu\text{m}^3$ of debris was found on the surface within the vicinity of the crater. The diameter of the ablation craters was approximately $6 \mu\text{m}$ and the ablation depth was of the order of $1 \mu\text{m}$. In these cases, the surface morphology suggested a violent and explosive removal of material. The debris patterns in the vicinity of the ablation craters were not reproducible. Figure 5 shows a typical laser-irradiated spot, using a $1 \mu\text{J}$ -pulse, and illustrates the nature of the refrozen material. Although this particular crater does not show it, some samples in this regime exhibited a high defect density in their centres, which presumably arose as a result of the refreeze-

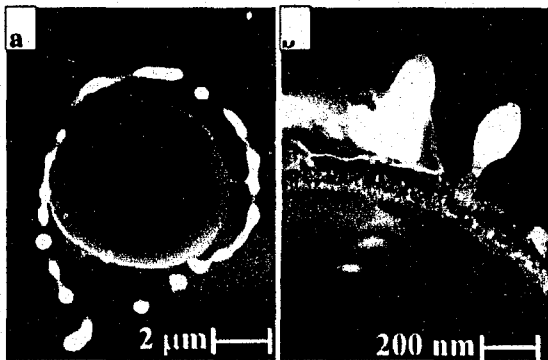


FIGURE 5 TEM images of: a a typical single-shot crater produced by a $1 \mu\text{J}$ -pulse of 130-fs duration in vacuum; and b blow-up of a rim from this regime. Several craters from this laser fluence bracket also exhibited refrozen material in their centres

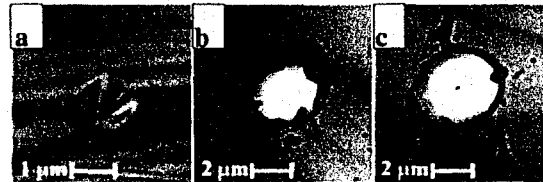


FIGURE 6 TEM images of single-shot craters produced by 10-ns pulses with energies of: a 180 nJ; b 250 nJ; and c 330 nJ

ing of molten silicon, which was not expelled from the crater. Only small variations in the size and depth of the craters were observed due to the laser intensity instabilities, and optical alignment was not as critical as in the lowest fluence range. Defocusing of the beam resulted in an increase of the spot size and therefore an increase in the lateral size of the ablation craters. Aberrations such as astigmatism will lead to asymmetric craters and debris patterns.

For the purposes of an initial comparison between nanosecond- and femtosecond-pulse irradiation, we also conducted a few selected investigations of nanosecond laser ablation of Si. Pulses of 790 nm-wavelength and of 10 ns-duration were obtained directly from the regenerative amplifier cavity when operated in a Q-switched regime. Pulse energies of 180, 250 and 330 nJ were utilized. TEM images of the resulting craters are shown in Fig. 6. The higher energy-damage threshold is expected in the case of irradiation with nanosecond pulses. The lowest energy pulse resulted in a weak feature of about $2.5 \mu\text{m}$ -diameter, with no discernable rim. The two higher-power pulses yielded crater diameters of 3.5 and $4 \mu\text{m}$ with approximately 500 nm-wide rims around the craters. Accounting for the higher threshold of the nanosecond irradiations, the lateral sizes of the features in the two temporal regimes were similar. In sharp contrast to the femtosecond studies, the rims for nanosecond irradiation were not uniform around the crater and there were many more droplets of expelled Si on the surrounding surfaces. Essentially, the higher-power craters were found to be much less regular than their femtosecond counterparts. Nevertheless, in the three cases investigated there was no evidence of extended defects resulting from the single-shot ablation process.

4 Discussion

The process of femtosecond laser ablation is still not fully understood, although a number of very illuminating experiments have been conducted in the past few years. For example, the work of von der Linde and co-workers has employed time-of-flight mass spectrometry studies [16] and time-resolved microscopy [17, 18] to supplement standard investigations and thereby gain new insights into the laser-solid interaction. Cavalleri et al. [16] have outlined five fluence intervals in the femtosecond laser interaction with materials (for 100 fs, 620 nm-pulses). For the lowest fluence range there is no melting, and the sample is heated via carrier relaxation on a picosecond timescale. Above a critical fluence ($150 \text{ mJ}/\text{cm}^2$ in Si) the temperature of the heated lattice exceeds the melting point, and at a somewhat higher fluence melting occurs via an ultrafast athermal process. For fluences exceeding the ab-

lation threshold (300 mJ/cm^2 in Si), macroscopic amounts of material leave the solid via a process involving a two-phase regime; a crater is produced on the surface. Under conditions of even more energetic pulses, the heating proceeds to a point where the expansion does not involve two phases.

Our results can be interpreted within this picture in a semi-quantitative way. For our lowest pulse energies, small, very shallow features were observed, which is consistent with the melting regime described in [16]. Near the damage threshold, the affected areas are very limited in depth since evaporation is a surface phenomenon. It is important to realize that due to the Gaussian laser beam, the target is exposed to a range of fluences [17], with off-axis areas experiencing a lower level of excitation due to the spatial intensity variation. Increasing the pulse energy leads to higher temperatures in the interaction volume and increased crater depth. For intermediate pulse energies, much deeper craters with a pronounced rim were observed in our experiments, consistent with an ablation regime [16, 18]. For the higher pulse energies utilized in this work, the laser fluence was above the limit for surface breakdown and plasma formation. Re-deposition of material during expansion leads to the irregular surface morphology around the craters in this fluence bracket. The rapid heating and cooling cycles are also most likely to be responsible for the defect concentration in the rims.

It should be noted, however, that the uncertainty in laser fluence in the present study is approximately 50% and renders precise comparisons with values obtained by other groups difficult. Absolute fluence determinations (as opposed to relative fluences) were not a key thrust of our first investigation, but rather detailed measurements on the final-state structures resulting from irradiations over a very broad range of laser-pulse energies. Moreover, the work of [16] and [18] was based on a different wavelength (620 nm), larger irradiated areas and typically shorter pulses interacting with semiconductor surfaces under ultrahigh vacuum conditions. Thus, the respective fluence scales cannot be considered identical. Nevertheless, in a follow-up experiment we measured the threshold obtained via back-extrapolating the squared diameter of the observed features [28, 31]. We obtained 300 mJ/cm^2 , in good qualitative agreement with the dynamical model discussed earlier. As an extension of the current study, detailed atomic force microscopy work aimed at determining the net volume removed (i.e. precise values for crater volume minus rim volume) would be very useful in future comparisons with the recent dynamical studies reported in the literature [16, 18]. This would serve to more definitively distinguish a transition between the melting and ablation fluence ranges in the context of our electron microscopy results.

Femtosecond laser machining is often described as essentially damage-free, in contrast to the results obtained with longer laser pulses in the nanosecond regime. In this study of single-shot femtosecond laser ablation of micron-sized features on silicon, we have not observed extended defects, even with detailed examinations using TEM techniques. Given the very large peak pressures predicted to be created during the ablation process, of the order of tens of GPa [18], it seems surprising that some evidence of extended defects has not been observed in the current study despite the ultrafast timescale involved. Assuming a sufficient coupling time to apply models

for dislocation formation [32], the pressure waves, which are driven into the substrate as a result of the ultrafast material removal, would exceed predicted critical pressures for the formation of extensive damage. The actual threshold for the creation of dislocations depends strongly on the validity of the assumption that the solid-liquid interface is an ideal source of extended defects. Even if it were not, we estimate that a critical pressure of only approximately 2 GPa would be required to nucleate dislocations in a perfect Si lattice [32]. Our experimental evidence from detailed electron microscopy is further supported by the recent work of Rousse et al. who used time-resolved X-ray diffraction to study athermal melting [21]. They report a maximum strain following athermal melting of InSb of 0.3%. This strain corresponds to a peak stress of less than 1 GPa, and would lie below the critical value needed to nucleate dislocations in InSb. Although this work concerned a binary semiconductor, our conclusions are qualitatively consistent with their observations. In addition, the recent paper by Loveridge-Smith et al. [22], using longer laser pulses, report very interesting results on the anomalous elastic response of silicon to stress in a nanosecond time frame. Further investigations aimed at relating ultrafast dynamical models to structural details of the final state of the residual material would be of considerable value.

Early work on Si using much longer laser pulses and large laser spot diameters revealed features on irradiated silicon surfaces [30]. In their initial study, optical microscopy and electron diffraction were used to assess the nature of the rings formed via approximately 30 ps-pulse irradiation at wavelengths of 266 and 532 nm. Liu et al. [30] associated these rings with amorphous silicon. In their second investigation, optical microscopy, time-resolved reflectivity, SEM and charged particle measurements were used to study melting and re-solidification of *n*-type (111) Si single crystal. Again, they discuss an amorphous region around the edges of the affected zone where the energy fluence only exceeded the melting threshold by a modest amount. In a very recent paper, Bonse et al. [29] also discuss amorphization of *n*-doped Si (111) for ultrashort laser-pulse irradiation in air. Their study, which puts a particular emphasis on multi-shot effects, spans a wide range of pulse lengths using laser focal diameters of tens of microns and laser center wavelengths close to our own. Our experiments found minimal evidence of amorphous material following laser irradiation of Si (100), although some amorphous-like layers were clearly observed for our 60 fs laser irradiations in air. We have also showed that there is a richness in the structure of the rims formed from femtosecond laser irradiation of Si (100), typically dominated by crystalline material comprising defects and small polycrystalline grains. There are several possible explanations for the different observations. The studies of [18, 29, 30] represent much larger spot-size irradiations on silicon surfaces, as opposed to our Si (100) work. Our laser-irradiated spots are typically only a few wavelengths of the laser light in dimension, which might influence the morphology of the observed features. Moreover, it has been reported that amorphization in silicon due to laser irradiation occurs more readily on (111) surfaces, as opposed to (100) surfaces. This has been explored by Yater and Thompson in a detailed study [33]. Liu et al. [30] have also provided clear evidence

for a higher amorphization threshold on Si(100) for 532-nm irradiation in their earlier report. In addition, the laser wavelengths of [18] and [30] (620 nm, 532 nm and 266 nm) are considerably shorter than in the present work, meaning that the absorption depths and cooling rates are different, although non-linear absorption effects must also be considered in this context. Finally, we note that distinguishing definitively between amorphous, polycrystalline and highly defective crystalline material is challenging on very thin samples. Thus, the comparisons between [18, 29, 30] and the current study appear reasonably consistent within the scopes of the respective works, although we might suggest further investigations on the nature of the residual surface material for Si(111) and Si(100) large-area single-shot irradiations at a wavelength of approximately 800 nm in both air and vacuum.

Our first exploratory experiments on single-shot nanosecond laser irradiation of Si did not exhibit extended defects either. The nanosecond laser studies were conducted under the conditions of creating similar-sized features to the femtosecond pulses in the intermediate fluence regime (50–300 nJ). It should be noted that the femtosecond and nanosecond irradiations are very different as regards the timescales for stress generation. In the case of femtosecond irradiation, there is a strong non-thermal component, whereas there is a thermal mechanism for longer pulse irradiation. It is possible that upon further increase in the nanosecond-pulse energy, corresponding to material removal comparable to the higher-energy femtosecond pulses (300 nJ – 1.9 µJ), extended defects would be observed; this remains to be explored. Moreover, in laser machining work, as opposed to surface marking, multiple-shot irradiation is involved. A comparative TEM-based study of short- and long-pulse irradiation under these conditions would be of practical value.

5 Conclusions

The present study has provided the first detailed results of a transmission electron microscopy evaluation of the residual state of Si(100) material after single-shot femtosecond laser irradiation. Our key thrust was a search for extended defects using TEM, in particular for the ablation fluences where high transient pressures are expected. The observations are generally in good agreement with several recent studies that have elucidated distinguishable regimes. The properties of the craters, as well as the surrounding rims, have been assessed. For pulse energies of less than 300 nJ and vacuum irradiation, the craters remained single-crystal and were essentially defect-free, except for the outer part of the rims where a relatively high defect density or polycrystalline content was observed. Even for higher pulse irradiations, no evidence of extended defects was found; the only defects present being those observed in the re-solidified material. This raises some questions regarding the peak pressures associated with ultrafast ablation processes. Future detailed AFM studies aimed at determining the actual volume removed in the interaction processes are also suggested. In addition to being of fundamental interest, our results contain valuable empirical information for practical consideration in the micromodification of materials using femtosecond light pulses. Issues such as the extent of material damage beyond the intended volume, as

well as structural and chemical changes resulting from ablation, are of immediate interest. Beyond the single-laser-pulse case, extensions to a detailed microscopic analysis of multi-shot induced effects would also be of value.

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REFERENCES

- 1 R.F. Wood, C.W. White, R.T. Young: *Semiconductors and Semimetals*, Vol. 23 (Academic, Orlando 1984)
- 2 S.A. Akhmanov, N.I. Koroteev, I.L. Shumay: *Nonlinear Optical Diagnostics of Laser-Excited Semiconductor Surfaces* (Harwood Academic, New York 1989)
- 3 D. Bäuerle: *Laser Processing and Chemistry* (Springer-Verlag, Berlin, Heidelberg, New York 2000), and references therein
- 4 P.P. Pronko, S.K. Dutta, D. Du, R.K. Singh: *J. Appl. Phys.* **78**, 6233 (1995)
- 5 X. Liu, D. Du, G. Mourou: *IEEE J. Quantum Electron.* **QE-33**, 1706 (1997)
- 6 X. Zhu, D.M. Villeneuve, A.Y. Naumov, S. Nikumb, P.B. Corkum: *Appl. Surf. Sci.* **152**, 138 (1999)
- 7 D. Ashkenasi, A. Rosenfeld, H. Rosenfeld, H. Varel, M. Wahmer, E.E.B. Campbell: *Appl. Surf. Sci.* **120**, 65 (1997)
- 8 H. Varel, D. Ashkenasi, A. Rosenfeld, M. Wahmer, E.E.B. Campbell: *Appl. Phys. A* **65**, 367 (1997)
- 9 S. Nolte, C. Momma, H. Jacobs, A. Tunnermann, B.N. Chichkov, B. Welleghausen, H. Welling: *J. Opt. Soc. Am. B* **14**, 2716 (1997)
- 10 S. Nolte, C. Momma, G. Kamlage, A. Ostendorf, C. Fallnich, F. von Alvensleben, H. Welling: *Appl. Phys. A* **68**, 563 (1999)
- 11 M. Lenzner, J. Krüger, W. Kautek, F. Krausz: *Appl. Phys. A* **69**, 465 (1999)
- 12 C.V. Shank, R. Yen, C. Hirlmann: *Phys. Rev. Lett.* **51**, 900 (1983); C.V. Shank, R. Yen, C. Hirlmann: *Phys. Rev. Lett.* **50**, 454 (1983)
- 13 H.W. Tom, G.D. Aumiller, C.H. Brito-Cruz: *Phys. Rev. Lett.* **60**, 1438 (1988)
- 14 M.C. Downer, C.V. Shank: *Phys. Rev. Lett.* **56**, 761 (1986)
- 15 K. Sokolowski-Tinten, J. Bialkowski, D. von der Linde: *Phys. Rev. B* **51**, 14186 (1995)
- 16 A. Cavalleri, K. Sokolowski-Tinten, J. Bialkowski, M. Schreiner, D. von der Linde: *J. Appl. Phys.* **85**, 3301 (1999)
- 17 K. Sokolowski-Tinten, J. Bialkowski, M. Doing, A. Cavalleri, D. von der Linde: *Phys. Rev. B* **58**, R11805 (1998)
- 18 K. Sokolowski-Tinten, J. Bialkowski, A. Cavalleri, D. von der Linde, A. Oparin, J. Meyer-ter-Vehn, S.I. Anisimov: *Phys. Rev. Lett.* **81**, 224 (1998); D. von der Linde, K. Sokolowski-Tinten: *Appl. Surf. Sci.* **154**, 1 (2000)
- 19 C. Rose-Petuck, R. Jimenez, T. Guo, A. Cavalleri, C.W. Siders, F. Ráksi, J.A. Squier, B.C. Walker, K.R. Wilson, C.P.J. Barty: *Nature* **398**, 310 (1999)
- 20 A. Cavalleri, C.W. Siders, F.L.H. Brown, D.M. Leitner, C. Tóth, J.A. Squier, C.P.J. Barty, K.R. Wilson, K. Sokolowski-Tinten, M. Horn von Hoegen, D. von der Linde, M. Kammler: *Phys. Rev. Lett.* **85**, 586 (2000)
- 21 A. Rousse, C. Rischel, S. Fourmaux, I. Uschmann, S. Sebban, G. Grillon, Ph. Balcou, E. Forster, J.P. Geindre, P. Audebert, J.C. Gauthier, D. Hulin: *Nature* **410**, 65 (2001)
- 22 A. Loveridge-Smith, A. Allen, J. Belak, T. Boehly, A. Hauer, B. Holian, D. Kalantar, G. Kyrala, R.W. Lee, P. Lomdahl, M.A. Meyers, D. Paisley, S. Pollaine, B. Remington, D.C. Swift, S. Weber, J.S. Wark: *Phys. Rev. Lett.* **86**, 2349 (2001)
- 23 P. Stampfli, K.H. Bennemann: *Phys. Rev. B* **49**, 7299 (1994); P. Stampfli, K.H. Bennemann: *Appl. Phys. A* **60**, 191 (1995)
- 24 R.F.W. Herrmann, J. Gerlach, E.E.B. Campbell: *Appl. Phys. A* **66**, 35 (1998)
- 25 S.I. Anisimov, N.A. Inogamov, A.M. Oparin, B. Rethfeld, T. Yabe, M. Ogawa, V.E. Fortov: *Appl. Phys. A* **69**, 617 (1999); N.A. Inogamov, Yu.V. Petrov, S.I. Anisimov, A.M. Oparin, N.V. Shaposhnikov, D. von der Linde, J. Meyer-ter-Vehn: *JETP Lett.* **69**, 310 (1999)

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- 26 P.L. Silvestrelli, A. Alavi, M. Parrinello, D. Frenkel: *Phys. Rev. Lett.* **77**, 3149 (1996)
- 27 T.H. Her, R.J. Finlay, C. Wu, E. Mazur: *Appl. Phys. A* **70**, 383 (2000)
- 28 J. Bonse, J.M. Wrobel, J. Krüger, W. Kautek: *Appl. Phys. A* **72**, 89 (2001)
- 29 J. Bonse, S. Baudach, J. Krüger, W. Kautek, M. Lenzner: *Appl. Phys. A* **74**, 19 (2002)
- 30 J.M. Liu, R. Yen, N. Bloembergen, R.T. Hodgson: *Appl. Phys. Lett.* **34**, 864 (1979); J.M. Liu, R. Yen, H. Kurz, N. Bloembergen: *Appl. Phys. Lett.* **39**, 755 (1981)
- 31 J.M. Liu: *Opt. Lett.* **7**, 196 (1982)
- 32 A. Kelly, N.H. MacMillan: *Strong Solids*, 3rd edn. (Oxford Science Publications, Oxford 1986)
- 33 J.A. Yater, M.O. Thompson: *Phys. Rev. Lett.* **63**, 2088 (1989)

Appendix C

Conference Contributions

Sub-wavelength surface structures on silicon irradiated by femtosecond laser pulses

T. H. R. Crawford, A. Borowiec, H. K. Haugen, Conference on Lasers and Electro-Optics (CLEO) CtuP40 (2004)

Imaging the strain fields resulting from femtosecond laser micromachining of semiconductors

A. Borowiec, H. K. Haugen, D. M. Bruce, D. T. Cassidy, Conference on Laser Ablation (COLA) ThPS95 (2003)

Subwavelength Ripple Formation on Surfaces of Compound Semiconductors Irradiated by Femtosecond Pulses

A. Borowiec, H. K. Haugen, Conference on Laser Ablation (COLA) MoPS94 (2003)

Wavelength dependence of the ablation threshold of InP

A. Borowiec, H. K. Haugen, Conference on Lasers and Electro-Optics (CLEO) 2003 CFF5 (2003)

Femtosecond micromachining of InP: analysis of ablation rates, morphology and residual strain

A. Borowiec, H. K. Haugen, Conference on Lasers and Electro-Optics (CLEO) CTuK37 (2002)

Imaging the strain fields resulting from femtosecond laser micromachining of semiconductors

A. Borowiec, H. K. Haugen, D. M. Bruce, D. T. Cassidy, Conference on Lasers and Electro-Optics (CLEO) CThS5 (2001)

Electron and atomic force microscopy studies of femtosecond laser machining of Si, GaAs and InP

A. Borowiec, M. MacKenzie, G.C. Weatherly, H. K. Haugen, Conference on Lasers and Electro-Optics (CLEO) CThL7 (2001)

Appendix D

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A. Borowiec, M. MacKenzie, G.C. Weatherly, H. K. Haugen, "Femtosecond laser pulse ablation of GaAs and InP : Studies utilizing scanning and transmission electron microscopy", Appl. Phys. A 77, 411 (2003)

A. Borowiec, M. MacKenzie, G.C. Weatherly, H. K. Haugen, "Transmission and Scanning Electron Microscopy Studies of Single Femtosecond Laser Pulse Ablation of Silicon", Applied Physics A, 76, 201 (2003)

J. Thøgersen, A. Borowiec, H. K. Haugen, F. E. McNeill, I. M. Stronach, "X-ray emission from femtosecond laser micromachining", Applied Physics A, 73, 361 (2001)

Also the following manuscript which was submitted to Applied Physics A: Rapid Communications, but has not yet been accepted.

A. Borowiec, M. Couillard, G. A. Botton, H. K. Haugen, "Sub-surface damage in indium phosphide caused by micromachining of grooves with femtosecond and nanosecond laser pulses"

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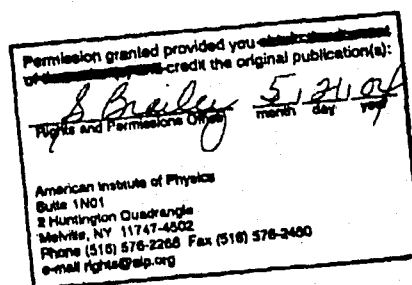
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References

- [1] I. B. Khaibulli, E. I. Shtyrkov, M. M. Zaripov, R. M. Bayazitov, and M. F. Galjantdinov: *Radiat. Eff.* **36**, 225 (1979)
- [2] P. L. Liu, R. Yen, N. Bloembergen, R. T. Hodgson: *Appl. Phys. Lett.* **34**, 864 (1979)
- [3] J. M. Liu, R. Yen, H. Kurz, N. Bloembergen: *Appl. Phys. Lett.* **39**, 755 (1981)
- [4] N. Bloembergen, R. K. Chang, S. S. Jha, C. H. Lee: *Phys. Rev.* **174**, 813 (1969)
- [5] C. V. Shank, R. Yen, C. Hirlimann: *Phys. Rev. Lett.* **51**, 900 (1983)
- [6] H. W. K. Tom, G. D. Aumiller, C. H. Brito-Cruz: *Phys. Rev. Lett.* **60**, 1438 (1988)
- [7] P. Saeta, J. K. Wang, Y. Siegal, N. Bloembergen, E. Mazur: *Phys. Rev. Lett.* **67**, 1023 (1991)
- [8] K. Sokolowski-Tinten, H. Schulz, J. Bialowski, D. von der Linde: *Appl. Phys. A* **53**, 227 (1991)
- [9] D. H. Reitze, X. Wang, H. Ahn, and M. C. Downer: *Phys. Rev. B* **40**, 11 986 (1989)
- [10] P. L. Silvestrelli, A. Alavi, M. Parrinello, D. Frenkel: *Phys. Rev. Lett.* **77**, 3149 (1996)
- [11] P. Stampfli, K. H. Bennemann: *Phys. Rev. B* **42**, 7163 (1990); *Phys. Rev. B* **46**, 10 686 (1992); *Phys. Rev. B* **49**, 7299 (1994)
- [12] D. Strickland, G. Mourou: *Opt. Commun.* **56**, 219 (1985)
- [13] G. Mourou: *Appl. Phys. B*, **65**, 205 (1997)
- [14] P. P. Pronko, S. K. Dutta, D. Du: *J. Appl. Phys.* **78**, 6233 (1995)
- [15] X. Liu, D. Du, G. Gouyou: *IEEE J. Quantum Electron.* **33**, 1706 (1997)
- [16] B. N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, A. Tünnermann: *Appl. Phys. A* **63**, 109 (1996)
- [17] A. Cavalleri, K. Sokolowski-Tinten, J. Bialkowski, M. Schreiner, D. von der Linde: *J. App. Phys.* **85**, 3301 (1999)
- [18] K. Sokolowski-Tinten, J. Bialkowski, M. Doing, A. Cavalleri, D. von der Linde: *Phys. Rev. B* **58**, R11 805 (1998)
- [19] K. Sokolowski-Tinten, J. Bialkowski, M. Doing, A. Cavalleri, D. von der Linde, A. Oparin, J. Mayer-ter-Vehn, S. I. Anisimov: *Phys. Rev. Lett.* **81**, 224 (1998)
- [20] D. von der Linde, K. Sokolowski-Tinten: *Appl. Surf. Sci.* **154-155**, 1 (2000)
- [21] C. R. Petrucci, R. Jimenez, T. Guo, A. Cavalleri, C. W. Siders, F. Raksi, J. A. Squire, B. C. Walker, K. R. Wilson, C. P. J. Barty: *Nature* **398**, 310, (March 1999)
- [22] A. H. Chin, R. W. Schoenlein, T. E. Glover, P. Balling, W. P. Leemans, C. V. Shank: *Phys. Rev. Lett.* **83**, 336 (1999)
- [23] A. Rousse, C. Rischel, S. Fourmaux, I. Uschmann, S. Sebban, G. Grillon, PH. Balcou, E. Forster, J.P. Geindre, P. Audebert, J.C. Gauthier, D. Hulin: *Nature* **410**, 65 (2001)
- [24] A. M. Lindenberg, I. Kang, S. L. Johnson, T. Missalla, P. A. Heimann, Z. Chang, J. Larsson, P. H. Bucksbaum, H. C. Kapteyn, H. A. Padmore, R. W. Lee, J. S. Wark, R. W. Falcone: *Phys. Rev. Lett.* **84**, 111 (2000)
- [25] J. Larsson, P. A. Heimann, A. M. Lindenberg, P. J. Schuck, P. H. Bucksbaum, R. W. Lee, H. A. Padmore, J. S. Wark, R. W. Falcone: *Appl. Phys. A* **66**, 587 (1998)
- [26] A. Cavalleri, C. W. Siders, F. L. H. Brown, D. M. Leitner, C. Tóth, J. A. Squier, C. P. J. Barty, K. R. Wilson, K. Sokolowski-Tinten, M. Horn von Hoegen, D. von der Linde, M. Kammmler: *Phys. Rev. Lett.* **85**, 586 (2000)
- [27] B. J. Siwick, J. R. Dwyer, R. E. Jordan, R. J. D. Miller: *Science* **302**, 1382 (2003)
- [28] W. Rozmus, V. T. Tikhonchuk, R. Cauble: *Phys. Plasmas* **3**, 260 (1996)
- [29] T. Q. Jia, R. X. Li, Z. Liu, Z. Z. Xu: *Appl. Phys. A* **74**, 503 (2002)

- [30] S. I. Anisimov, N. A. Inogamov, A. M. Oparin, B. Rethfeld, T. Yabe, M. Ogawa, V. E. Fortov: *Appl. Phys. A* **69**, 617 (1999)
- [31] N. A. Inogamov, Yu. V. Petrov, S. I. Anisimov, A. M. Oparin, N. V. Shaposhnikov, D. von der Linde, J. Meyer-ter-vehn: *JETP Letters* **69**, 310 (1999)
- [32] A. Miotello, R. Kelly: *Appl. Phys. Lett.* **67**, 3535 (1995)
- [33] S. Siano, R. Pini, R. Salimbeni: *Appl. Phys. Lett.* **74**, 1233 (1999)
- [34] A. Loveridge-Smith, A. Allen, J. Belak, T. Boehly, A. Hauer, B. Holian, D. Kalantar, G. Hyrala, R. W. Lee, P. Lomdahl, M. A. Meyers, D. Paisley, S. Pollaine, B. Remington, D. C. Swift, S. Weber, J. S. Wark: *Phys. Rev. Lett.* **86**, 2349 (2001)
- [35] V. I. Emel'yanov, D. V. Babak: *Appl. Phys. A* **74**, 797 (2002)
- [36] R. F. W. Herrmann, J. Gerlach, E. E. B. Campbell: *Appl. Phys. A* **66**, 35 (1998)
- [37] L. V. Zhigilei, B. J. Garrison: *J. Appl. Phys.* **88**, 1281 (2000)
- [38] D. Perez, L. J. Lewis: *Phys. Rev. Lett.* **89**, 255504 (2002)
- [39] C. Shafer, H. M. Urbassek, L. V. Zhigilei: *Phys. Rev. B* **66**, 115404 (2002)
- [40] D. S. Ivanov, L. V. Zhigilei: *Phys. Rev. Lett.* **91**, 105701 (2003)
- [41] D. Perez, L. J. Lewis: *Phys. Rev. B* **67**, 184102 (2003)
- [42] P. Lorazo, L. J. Lewis, M. Meunier: *Phys. Rev. Lett.* **91**, 225502 (2003)
- [43] D. Bäuerle: "Laser Processing and Chemistry" 3rd Edition, Springer-Verlag Berlin Heidelberg 2000
- [44] D. H. Reitze, T. R. Zhang, Wm. M. Wood, M. C. Downer: *J. Opt. Soc. Am. B* **7**, 84 (1990)
- [45] K. Sokolowski-Tinten, D. von der Linde: *Phys. Rev. B* **61**, 2643 (2000)
- [46] N. M. Bulgakova, R. Stoian, A. Rosenfeld, I. V. Hertel, E. E. B. Campbell: *Phys. Rev. B* **69**, 054102 (2004)
- [47] I. L. Shumay, U. Höfer: *Phys. Rev. B* **53**, 15878 (1996)
- [48] J. Bonse, S. M. Wiggins, J. Solis: accepted for publication in *Appl. Phys. A* (2004)
- [49] J. M. Moisson, M. Bensoussan: *J. Vac. Sci. Technol.* **21**, 315 (1982)
- [50] M. Raff, M. Schütze, C. Trappe, R. Hannot, H. Kurz: *Phys. Rev. B* **50**, 11031 (1994)-I
- [51] J. Kanasaki, N. Mikasa, K. Tanimura: *Phys. Rev. B* **64**, 035414 (2001)
- [52] B. Dubreuil, T. Gibert: *J. Appl. Phys.* **76**, 7545 (1994)
- [53] J. Bonse, J. M. Wrobel, J. Krüger, W. Kautek: *Appl. Phys. A* **72**, 89 (2001)
- [54] M. Argument, S. Kirkwood, K. Chau, A. van Popta, Y. Tsui, R. Fedosejevs: *Tech. Digest SPIE: Proc. Opto-Canada TD01*, pp. 196-199 (2002)
- [55] J. Bonse, J. M. Wrobel, K. -W. Brzezinka, N. Esser, W. Kautek: *Appl. Surf. Sci.* **202**, 272 (2002)
- [56] J. Bonse, M. Lenzner, J. Krüger: "Modification and ablation of semiconductors by femtosecond laser pulses", *Recent Res. Devel. Applied Phys.* 5 (part II) pp. 437-461, Trivandrum, India, Transworld Research (2002)
- [57] A. Borowiec, M. MacKenzie, G.C. Weatherly, H. K. Haugen: *Appl. Phys. A* **77**, 411 (2003)
- [58] A. Borowiec, H. K. Haugen: *Appl. Phys. Lett.* **82**, 4462 (2003)
- [59] A. M. Ozkan, A. P. Malshe, T. A. Railkar, W. D. Brown, M. D. Shirk, P. A. Molian: *Appl. Phys. Lett.* **75**, 3716 (1999)
- [60] F. Costache, M. Henyk, J. Reif: *Appl. Surf. Sci.* **186**, 352 (2002)
- [61] M. Henyk, N. Vogel, D. Wolframm, A. Tempel, J. Reif: *Appl. Phys. A* **69** [suppl], S355 (1999)
- [62] Q. Wu, Y. Ma, R. Fang, Y. Liao, Q. Yu, X. Chen, K. Wang: *Appl. Phys. Lett.* **82**, 1703 (2003)
- [63] F. Costache, M. Henyk, J. Reif: *Appl. Surf. Sci.* **208-209**, 485 (2003)
- [64] N. Yasumaru, K. Miyazaki, J. Kiuchi: *Appl. Phys. A* **76**, 983 (2003)
- [65] Z. Guosheng, P. M. Fauchet, A. E. Siegman: *Phys. Rev. B* **26**, 5366 (1982)
- [66] J. F. Young, J. E. Sipe, H. M. van Driel: *Phys. Rev. B* **30**, 2001 (1984)
- [67] G. Dumitru, V. Romano, H. P. Weber, M. Sentis, W. Marine: *Appl. Phys. A* **74**, 729 (2002)
- [68] A. Borowiec, H. K. Haugen: *Appl. Phys. A* **79**, 521 (2004)
- [69] A. Borowiec, D. M. Bruce, D. T. Cassidy, H. K. Haugen: *Appl. Phys. Lett.* **83**, 225 (2003)
- [70] M. Prasad, H. E. Ruda, J. J. Dubowski: *J. Vac. Sci. Technol. B* **15**, 2046 (1997)

- [71] J. M. Wrobel, C. E. Moffitt, D. M. Wieliczka, J. J. Dubowski, J. W. Fraser: *Appl. Surf. Sci.* **127-129**, 805 (1998)
- [72] R. Matz, H. Weber, G. Weimann: *Appl. Phys. A* **65**, 349 (1997)
- [73] N. Bärsch, K. Körber, A. Ostendorf, K.H. Tönshoff: *Appl. Phys. A* **77**, 237 (2003)
- [74] E. Dupont, X. Zhu, S. Chiu, S. Moisa, M. Buchanan, M. Gao, H. C. Liu, P. B. Corkum: *Semicond. Sci. Technol.* **15**, L15 (2000)
- [75] D. Altenbernd, U. Teubner, P. Gibbon, E. Foster, P. Audebert, J-P. Geindre, J. C. Gauthier, G. Grillon, A. Antioetti: *J. Phys. B*, **30**, 3969 (1997)
- [76] M. Schnurer, M. P. Kalashnikov, P. V. Nickles, Th. Schlegel, W. Sander, N. Demchenko, R. Nolte, P. Ambrosi: *Phys. Plasmas* **2**, 3106 (1995)
- [77] J. D. Kmetec, C. L. Gordon, J. J. Macklin, B. E. Lemoff, G. S. Brown, S. E. Harris: *Phys. Rev. Lett.* **68**, 1527 (1992)
- [78] J. Thøgersen, A. Borowiec, H. K. Haugen, F. E. McNeill, I. M. Stronach: *Applied Physics A*, **73**, 361 (2001)
- [79] M. Hagedorn, J. Kutzner, G. Tsilimis, H. Zacharias: *Appl. Phys. B* **77**, 49 (2003)
- [80] A. Thoss, M. Richardson, G. Korn, M. Faubel, H. Stiel, U. Vogt, T. Elsaesser: *J. Opt. Soc. Am. B* **20**, 224 (2003)
- [81] Y. Jiang, T. Lee, C. G. Rose-Petruck, *J. Opt. Soc. Am. B* **20**, 229 (2003)
- [82] A. H. Firester, M. E. Heller, P. Sheng: *Appl. Opt.* **16**, 1971 (1977)
- [83] J. M. Khosroffian, B. A. Garetz: *Appl. Opt.* **22**, 3406 (1983)
- [84] H. R. Bilger, T. Habib: *Appl. Opt.* **24**, 686 (1985)
- [85] J.M. Liu: *Opt. Lett.* **7**, 196 (1982)
- [86] J. C. Diels, W. Rudolph: "Ultrashort laser pulse phenomena" Academic Press (1996)
- [87] R. Trebino: "Frequency-Resolved Optical Grating: The Measurement of Ultrashort Laser Pulses", Kluwer Academic Publishers, Boston 2000
- [88] K. A. Briggman, L. J. Richter, J. C. Stephenson: *Opt. Lett.* **26**, 238 (2001)
- [89] M.W. Phaneuf: *Micron* **30**, 277-288 (1999)
- [90] P. D. Colbourne, D. T. Cassidy: *IEEE J. Quantum Electron.* **29**, 62 (1993)
- [91] D. T. Cassidy: *Mat. Sci. Eng. B* **91-92**, 2 (2002)
- [92] A. Borowiec, M. MacKenzie, G. C. Weatherly, H. K. Haugen: *Appl. Phys. A* **76**, 201 (2003)
- [93] J. Jia, M. Li, C. V. Thompson: *Appl. Phys. Lett.* **84**, 3205 (2004)
- [94] F. Costache, S. Kouteva-Arguirova, J. Reif, The 7th International Conference on Laser Ablation Preceedings, paper ThPS20 (2003)
- [95] F. Costache, S. Kouteva-Arguirova, J. Reif: *Gettering and Defect Engineering in Semiconductor Technology Solid State Phenomena* **95-96**, 635 (2004)
- [96] T. H. R. Crawford, A. Borowiec, H. K. Haugen, "Sub wavelength surface structuring on silicon irradiated by femtosecond laser pulses", CLEO/IQEC and PhAST Technical Digest on CD-ROM (The Optical Society of America, Washington, DC, 2004) CtuP40
- [97] S. Nolte, C. Momma, G. Kamlage, A. Ostendorf, C. Fallnich, F. von Alvensleben, H. Welling: *Appl. Phys. A* **68**, 563 (1999)
- [98] T. Crawford, A. Borowiec, H. K. Haugen: published on-line 31 August 2004, *Appl. Phys. A* (2004)
- [99] M. Lenzner, J. Krüger, S. Sartania, Z. Cheng, Ch. Spielmann, G. Mourou, W. Kautek, F. Krausz: *Phys. Rev. Lett.* **80**, 4076 (1998)
- [100] R. Stoian, M. Boyle, A. Thoss, A. Rosenfeld, G. Korn, I. V. Hertel, E. E. B. Campbell: *Appl. Phys. Lett.* **80**, 353 (2002)
- [101] T. U. Choi, D. J. Hwang, C. P. Grigoropoulos: *Appl. Surf. Sci.* **197-198**, 720 (2002)
- [102] M. Spyridaki, E. Koudoumas, P. Tzanetakis, C. Fotakis, R. Stoian, A. Rosenfeld, I. V. Hertel: *Appl. Phys. Lett.* **83**, 1474 (2003)
- [103] A. M. Weiner: *Rev. Sci. Instrum.* **71**, 1929 (2000)

- [104] M. Lapczynya, K. P. Chen, P. R. Herman, H. W. Tan, R. S. Majoribanks: Appl. Phys. A **69**, S883 (1999)
- [105] C. B. Schaffer, A. Brodeur, J. F. Garca, E. Mazur: Opt. Lett. **26**, 93 (2001)
- [106] M. B. Agranat, S. I. Ashitkov, V. E. Fortov, A. V. Kirillin, A. V. Kostanovskii, S. I. Anisimov, P. S. Kondratenko: Appl. Phys. A **69**, 637 (1999)
- [107] V. V. Temnov, K. Sokolowski-Tinten, P. Zhou, D. von der Linde: Appl. Phys. A **78**, 483 (2004)