Investigation into surface texturing by magnetic field assisted laser-produced plasma

Hamid Farrokhi

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**INVESTIGATION INTO SURFACE TEXTURING BY
MAGNETIC FIELD ASSISTED LASER-PRODUCED PLASMA**

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BY MAGNETIC FIELD ASSISTED LASER-
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**HAMID FARROKHI
SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING
2013**

**INVESTIGATION INTO SURFACE TEXTURING
BY MAGNETIC FIELD ASSISTED LASER-
PRODUCED PLASMA**

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*Hamid Farrokhi
NTU, Singapore
March, 2013*

Abstract

In this thesis, we investigated the irradiation of silicon with infrared fiber laser ($\lambda = 1090$ nm) at energy densities exceeding the ablation threshold. We characterize the irradiated surface and properties of the ejected material showing the big volume of silicon oxide at the rim of the irradiated line. The results showed that the infrared fiber laser could not be regarded as a suitable tool for the purpose of micromachining and effective ablation of silicon. Seeking for reason revealed that silicon is highly transparent to the infrared wavelength of fiber laser ($\lambda=1090$ nm). Thus it was proposed to make use of the laser to texture silicon surface rather than to ablate it.

Since surface texturing is an important research area in the field of laser material processing with a broad range of applications, thus we investigated silicon surface texturing using infrared fiber laser in a background gas. Micron and submicron texturing of silicon by laser ablation is of great interest due to its wide use in microelectronics and solar cells. However, the approaches are based on the target *ablation* and redistribution of melt materials.

Hardly any reports can be found in the public domain on the use of non-ablative laser surface texturing to form uniform patterns. As it is said earlier silicon is known to be highly transparent to the infrared wavelength of fiber laser ($\lambda=1090$ nm), so fiber laser is not regarded as a suitable tool for ablative texturing of silicon. Thus we developed a technique to irradiate and pattern silicon surface in O_2 gas environment using various laser parameters (laser power and beam dwell time). With this technique, we succeeded in patterning Si surface by *non-ablative* laser texturing using continuous wave fiber laser ($\lambda=1090$ nm).

We explained the non-ablative surface texturing in terms of laser-induced localized thermal oxidation. However, the proposed mechanism is based on qualitative analyses only. Thus we have chosen finite element method for thermal modeling of phenomenon in order to understand the mechanism of non-ablative texturing. The analysis shows the technique is based on laser-

induced thermal oxidation. The numerical analysis was used to map laser parameters (laser power vs dwell time) for non-ablative laser texturing of silicon. It shows the effective oxidation zone to produce regular bumps on silicon.

Since non-ablative laser surface texturing could be based on thermal or non-thermal mechanism and it has not been well studied, we investigated non-ablative Si surface texturing based on laser induced non-thermal oxidation phenomenon as a new technique of surface structuring. We used low repetition rate (1 kHz) of femtosecond laser pulses with negligible thermal accumulation and succeeded in non-ablative direct writing of silicon surface. The approach is shown to be based on laser-induced localized non-thermal oxidation of silicon that will be explained in details.

Finally we have investigated and developed magnetic field assisted laser ablation as a novel technique of surface structuring. The use of a magnetic field with laser produced plasma (LPP) is of great interest in basic and engineering research since a magnetic field can effectively control the dynamic properties of this transient and energetic plasma. In engineering research, most studies have been conducted on pulsed laser deposition (PLD) techniques to get the particulate-free films. Some researchers have also investigated magnetic field assisted laser welding and hardening to increase penetration depth, to unify elements distribution and to favor pore outgassing. However, hardly any studies can be found in the public domain on magnetic field assisted laser micromachining of materials and its effect on laser ablation efficiency.

In the present study, we have studied the magnetic field-assisted laser ablation of materials irradiated by nanosecond (355nm, 20ns) and femtosecond (775 nm, 150 fs) lasers. Silicon has been initially chosen for the study since it is an important semiconductor material in electronic, solar cells, and sensors. Stainless steel 304 and titanium alloy (Ti4Al6V) were also chosen to examine applicability of the technique in surface structuring of various materials. The solenoid copper coil was designed and fabricated to apply an axial magnetic

field ($B \perp$ to target plane and $\parallel$ to laser beam) with various field strength. The results showed the remarkable effect of the external magnetic field on the ablation efficiency. However, laser ablation efficiency under the magnetic field in ns laser is much great comparing with that in femtosecond laser ablation. This might be due to no laser-plasma interactions in the fs irradiation. The plasma cools quickly since no further energy is supplied by the fs laser. However, a fraction of the laser energy is absorbed by the ns-induced plasma that results in greater temperature and electron density of the plasma.

Magnetohydrodynamic (MHD) analysis showed that the magnetic field confines the induced plasma. The ns-induced plasma, which is denser and hotter comparing with the fs-induced plasma, becomes denser and hotter under the external magnetic field. This leads to efficient deposition of plasma thermal energy and high laser ablation efficiency in ns laser ablation, as shown in the results. It is expected that this technique would have potential applications in the laser processing of hard-to-ablate materials, laser cutting, laser welding, etc.

In this thesis, we hope to give the reader an impression of the exciting field of non-ablative laser surface texturing based on laser-induced thermal and non-thermal oxidation, and novel technique of magnetic field assisted laser surface texturing.

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List of Acronyms

NSOM: near field optical microscope

LPP: laser produced plasma

PLD: pulsed laser deposition

MHD: magnetohydrodynamics

CW: continuous wave

Nd:YAG: neodymium-doped yttrium aluminum garnet

Er:YAG: erbium-doped yttrium aluminum garnet

Nd:YLF: neodymium-doped yttrium lithium fluoride

HAZ: heat affected zone

UV: ultraviolet

DUV: deep ultraviolet

EUV: extreme ultraviolet

PZT: lead zirconium titanate

NA: numerical aperture

CCD: charge-coupled device

CVD: chemical vapor deposition

MLA: micro lens array

CPLA: contact particle lens array

SEM: scanning electron microscope

LIPSS: laser induced periodic surface structures

SHIM: scanning helium ion microscope

SEW: surface electromagnetic wave

TEM: transverse electric mode or transmission electron microscope

DPSS: diode-pumped solid state

XRD: X-ray diffraction

EDX or EDS: energy dispersive X-ray spectroscopy

STEM: scanning transmission electron microscope

XPS: X-ray photoelectron spectroscopy

KE: kinetic energy

BE: binding energy
AFM: atomic force microscopy
AM: amplitude modulated
FM: frequency modulated
PDE: partial differential equation
CA: contact angle
SS: stainless steel
HTS: high temperature superconductor
HLAW: hybrid laser-arc welding

Chapter 1: Introduction

1.1. Background and Motivation

The increasing demand for miniaturizing the components and functionalizing their surfaces has generated worldwide efforts towards the development of laser surface structuring. Since silicon is as a core semiconductor material with broad applications in electronics, solar cells and sensors, we have chosen to study and develop new techniques for its laser surface structuring and machining under various conditions.

Firstly, fiber laser ($\lambda = 1090 \text{ nm}$) as a new laser generation has been selected to study the feasibility of silicon micromachining. The results showed that the infrared fiber laser could not be regarded as a suitable tool for the purpose of micromachining and material removal of silicon. Since silicon is known to be highly transparent to the infrared wavelength of fiber laser ($\lambda=1090 \text{ nm}$). Thus it was proposed to make use of infrared laser to texture silicon surface rather than to machine it. Thus, investigation have been carried out to develop a technique for silicon laser surface structuring using the infrared fiber laser.

Surface texturing is an important research area in the field of laser material processing with a broad range of applications in electronics, solar cells, and sensors. Micron and submicron texturing of silicon by laser ablation [1-5] has drawn strong interest due to its wide use in microelectronics and solar cells. Several groups have also reported use of pulsed lasers to produce grooves [6] or pits [7] on surfaces of many other materials such as Ge [8], metals [9] and thin films [10] under diverse experimental conditions. Near-field enhanced laser irradiation with micro-nano sized spheres [11, 12] and near field scanning optical microscope (NSOM) [13, 14] are used to form micron, submicron, and nano patterns, but the approaches are also based on the target *ablation* and redistribution of melt materials.

Hardly any reports can be found in the public domain on use of non-ablative laser surface texturing to form uniform patterns. As it is said earlier silicon is known to be highly transparent to the infrared wavelength of fiber laser ($\lambda=1090$ nm), so fiber laser is not regarded as a suitable tool for ablative texturing of silicon. Thus the aim of this investigation is to develop a technique to pattern silicon surface using the fiber laser. With this aim, we developed a novel technique to pattern Si surface by *non-ablative* laser texturing using continuous wave fiber laser ($\lambda=1090$ nm) [15, 16].

We investigated and explained the non-ablative surface texturing in terms of laser-induced localized thermal oxidation. However, the proposed mechanism is based on qualitative analyses only. Thus we have chosen finite element method for thermal analysis of the phenomenon to gain better understanding of the non-ablative texturing mechanism. Since it has been used successfully to study laser processing of materials [17-22] and in particular thermal oxidation of Si [23-25]. The analysis showed the technique is based on thermal laser-induced oxidation.

Non-ablative laser surface texturing could be based on thermal or non-thermal mechanism and it has not been well studied. Thus we set the study on non-ablative texturing of silicon surface based on non-thermal mechanism as second aim of this investigation. We used low repetition rate (1 kHz) of femtosecond laser pulses with negligible thermal accumulation and succeeded in non-ablative direct writing of silicon surface. The approach is shown to be based on laser-induced localized non-thermal oxidation of silicon that will be explained in details.

Finally we have carried out the investigation on magnetic field assisted laser ablation as third aim of the study. The use of a magnetic field with laser produced plasma (LPP) is of great interest in basic and engineering researches since a magnetic field can be used to effectively control the dynamic properties of this transient and energetic plasma. In engineering research, most studies have been conducted on pulsed laser deposition (PLD) techniques to get the

particulate-free deposition and . The effect of an external electric field on Si LPP in order to get debris free surfaces was well studied [26]. Some researchers have also investigated on magnetic field assisted laser welding and hardening to increase penetration depth, to unify elements distribution and to favor pore outgassing [27-30]. However, hardly any studies can be found on magnetized laser micromachining of materials and its effect on ablation efficiency.

Thus we studied and developed the magnetic field-assisted ns and fs laser ablation of silicon, stainless steel, and titanium alloy (Ti4Al6V) by introducing an axial magnetic field ($B \perp$ to target plane and $\parallel$ to laser beam). Firstly, the surfaces were irradiated using nanosecond laser (355 nm, 20 ns) in line and pocket schemes. SEM and the profile images showed very high laser ablation efficiency. Later, fs laser (775 nm, 150 fs) was used to irradiate silicon surface. It is found that laser ablation efficiency in fs laser is lower comparing with that in ns laser. Since the induced plasma properties in fs and ns irradiation are different, this could result in different laser ablation efficiency. This is because of no laser-plasma interactions in the fs irradiation. The plasma cools quickly since no further energy is supplied by the fs laser. However, a fraction of the laser energy is absorbed by the ns-induced plasma that results in greater temperature and electron density.

Magnetohydrodynamic (MHD) analysis showed that the magnetic field confines the induced plasmas. Thus the ns-induced plasma becomes denser and hotter under the influence of the external magnetic field. This leads to efficient plasma heating and high laser ablation efficiency in ns laser ablation, as shown in the results. It is expected that this technique would have potential applications in the laser processing of hard-to-ablate materials, laser cutting, laser welding, etc.

In this thesis, we hope to give the reader an impression of techniques for non-ablative laser surface texturing based on laser-induced thermal/nonthermal oxidation, and ns/fs laser material processing under the influence of external magnetic field.

1.2. Objectives and Scopes

In the study, the objective is to explore and develop new techniques for laser surface structuring, but not to modify the existing techniques in the field.

On the basis of this objective we have reviewed the existing micro/nano laser surface structuring techniques and came up with two novel techniques for laser surface structuring.

(1) Non-ablative surface texturing.

Literature review showed laser surface texturing based on ablation has been widely used, but hardly any report can be found on non-ablative laser surface texturing.

(2) Magnetic field assisted surface structuring.

Literature review also showed the use of a magnetic field with laser produced plasma (LPP) is of great interest since a magnetic field can be used to effectively control the dynamic properties of this transient and energetic plasma. Besides its basic research importance, the effect of a magnetic field on the expansion dynamics of LPP has also gained importance in applied research such as pulsed laser deposition (PLD) techniques, magnetic field assisted laser welding and hardening. However, no report has been found on magnetic field assisted laser surface structuring.

Thus, a systematic investigation was carried out, and some original contributions were achieved, e.g., the development of non-ablative (thermal/non-thermal) laser surface texturing of silicon and magnetic field assisted laser (ns/fs) machining.

The scopes of this study are as the following:

- (1) Non-ablative surface texturing of silicon based on laser induced thermal oxidation
- (2) Non-ablative surface texturing of silicon based on laser induced non-thermal oxidation
- (3) Magnetic field assisted nanosecond laser ablation of materials
- (4) Magnetic field assisted femtosecond laser ablation of materials

1.3. Layout

Chapter 2 reviews historical development of lasers, their fundamentals, and type of lasers for materials processing. It also describes the common issues on laser processing of materials and explains diffraction limit of lasers and summarizes the current techniques in literatures to overcome it for micro/nano laser processing of the materials. Laser-induced plumes, their dynamics and effects on laser-material interaction are also reviewed in chapter 2.

Chapter 3 describes the materials and the main experimental methods used in the study.

Chapter 4 presents the results of fiber laser micromachining of silicon and how the results brought the idea of using the infrared fiber laser ($\lambda = 1090$ nm) to texture silicon surface through non-ablative techniques. It also explains the thermal/non-thermal oxidation of silicon that has been used for non-ablative surface texturing. The results of magnetic field assisted ns and fs laser ablation of materials are also presented and explained in chapter 4.

Chapter 5 summarizes the main results obtained in this thesis and proposes future avenues of research to address several still unanswered questions regarding non-ablative laser surface texturing and magnetized laser ablation of materials.

Chapter 2: Literature Review

2.1. Introduction

This chapter will consider some of historical development of lasers, their fundamentals, and types of lasers that are relevant to the understanding of lasers and their applications for material processing. We will describe the common issues on laser processing of materials such as effect of wavelength and implication on delivery of laser beam energy, effects of pulse duration, thermal and non thermal effects of pulse duration.

We will explain diffraction limit of lasers and summarize the current proposed techniques in literatures to overcome it. We will then review laser direct writing of micro/nano structures; laser direct writing beyond diffraction limit and laser induced periodic surface structures. Finally, laser induced plumes, their dynamics and effects on laser-material coupling will be explained.

2.2. Fundamental of Laser

Laser is a short form for Light Amplification by Stimulated Emission of Radiation. The foundation for present view of laser was proposed by Max Planck as the radiant energy emitted in discrete unit or quanta [31, 32]. Regarding to those findings, laser can be considered as an electromagnetic wave which is propagating with velocity of $c_0 = 299792458 m/s$ in vacuum. It is composed of electric and magnetic field oscillating vertically to each other and to the direction of propagation, as shown in Figure 2.1.

Wavelength (λ) and frequency (ν) of light are mutual parameters which are linked by the equation:

$$c_0 = \lambda \cdot \nu \quad (2.1)$$

Figure 2.1 Electromagnetic wave propagation and optical spectrum [33]

If the electromagnetic radiation interacts with atoms, ions or molecules, it will transfer the minimal energy amount $\Delta E = h\nu$, where h is the Planck's constant ($h = 6.6260755 \times 10^{-34} \text{ J} \cdot \text{s}$). Therefore, electromagnetic radiation is the flow of these minimal energy packages called photons [32, 33].

To understand how laser is emitted, it should be considered that atoms, molecules, crystals and any other solid-state matter are quantized system and characterized by electron shells introduced in Bohr model. Thus in order to picture the different energetic states, an energy-level diagram is used in Figure 2.2. If such system receives energy by a collision or interaction with other electrons, atoms or photons, the system is transferred into an excited state. Transferred energy by photons is called absorption. For excitation from the ground state to an excited state, the transferred energy has to be large enough to overcome the energy gap.

If an electronic system is excited to a higher energy state (E_2), life time of this state depends on the atomic species involved. Some levels have long life times measured in seconds, whereas others are relatively short, of the order of nanoseconds or less [32, 34]. Electron energy will eventually drop to the lower

energy state (E_1). The energy difference between transition levels ΔE is emitted as a photon with frequency of ν_{12} :

$$\Delta E = E_2 - E_1 = h\nu_{12} \quad (2.2)$$

Figure 2.2 Illustration of absorption and emission of radiation [33]

Since this transition takes place statistically in time and space, this kind of energy emission is called ‘spontaneous emission’. The processes of absorption and spontaneous emission are totally reversible.

Another interaction process shown in Figure 2.2, is called ‘stimulated emission’, which is necessary for lasing. This process was predicted by Albert Einstein in 1917 [35], but it was practically realized by Theodore Miaman in 1960. Stimulated emission can occur when photons interact with an electronic system in an excited state (E_2) of the same frequency (ν_{12}) as mentioned in Equation (2.2). This photon stimulates the emission process. The essential for any laser system to operate is that the emitted photon is transferring in the same direction as the initial one and its wave is in phase (coherent) with the stimulating photon to make amplification possible.

However, another side of laser phenomenon is ‘population inversion’ within the active lasing medium which is required to be considered. Under normal condition, known as the thermodynamic equilibrium, electronic quantized systems tend to get back to their most stable state which is their lowest available energy level, the system’s ground state. If the laser system with two levels is considered as a lasing media with N_1 atoms in the ground state and N_2 atoms in the excited state, the distribution of the atoms among the two levels can be mathematically expressed in terms of a ‘Boltzmann distribution’ [33]:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{k_B T}} = e^{-\frac{h\nu}{k_B T}} \quad (2.3)$$

where k_B is the Boltzmann constant ($k_B = 1.380658 \times 10^{-23}$ J/K) and T the temperature in Kelvin (K). The ratio of N_2/N_1 will always be < 1 , so that an initial interacting photon is high possible to be absorbed by the atoms of level 1 (N_1) than by the atoms of level 2 (N_2). Under these conditions, spontaneous emission dominates and no light amplification can be achieved.

Population inversion (i.e. $N_2 > N_1$) is a vital requirement to the laser system so that stimulated emission is more likely than absorption and subsequent spontaneous emission. Light amplification takes place due to the difference between stimulated emission and absorption. The subsequent equations describe the probability of absorption, spontaneous and stimulated emission during interaction with radiation of spectral density $\rho(\nu)$. The number of transitions dN in the time dt can be described by [31, 33]:

$$dN_{12,abs} = B_{12}\rho(\nu)N_1dt \quad (\text{absorption}) \quad (2.4)$$

$$dN_{21,spot} = A_{21}N_2dt \quad (\text{spontaneous emission}) \quad (2.5)$$

$$dN_{21,stim} = B_{21}\rho(\nu)N_2dt \quad (\text{stimulated emission}) \quad (2.6)$$

where A and B are the ‘Einstein coefficients’ representing the transition probability of spontaneous emission (A) and stimulated emission (B) which are related by:

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c_0^3} \quad (2.7)$$

Thus it is notable that the probability of spontaneous emission increases proportionally to ν^3 compared to the probability of stimulated emission. This physical dependence defines the problem to design a light amplifying system that emits short wavelength radiation (high frequency radiation).

2.3. Types of Laser

Albert Einstein first explained the theory of stimulated emission in 1917, which led to the invention of laser. However, it was in late 1940s and 1950s that scientists and engineers did extensive work to realize a practical device based on the principle of stimulated emission. The first laser in the world was demonstrated by Theodore Maiman in 1960 using a ruby crystal as lasing medium.

The development of lasers has been a shiny point in the history of science and engineering. It has led to totally new kind of system for wide range of applications. During the sixties, lots of efforts have been conducted on the basic development of almost all types of lasers as well as the practical application in defense and industry. In early seventies, megawatt class carbon dioxide gas laser was successfully developed. Other new types of laser such as chemical lasers, free electron and X-ray laser took a little bit longer to be developed because of requirement of multidisciplinary approach.

Before reviewing the type of lasers, we have briefly summarized the essential practical requirements to make lasing happens. In order to generate a coherent and highly oriented beam, it is essential that the light amplification takes place in an optical system. Such system is generally composed of mirrors arranged on opposite sides of laser medium to oscillate the radiation within the laser resonator or laser cavity. Simple design of a laser resonator is shown in Figure 2.3. One of the mirrors is totally reflective ($R = 100\%$), while the other is partially reflective to let a portion of the light leak out of the cavity, thereby forming the laser beam.

Figure 2.3 Principle illustration of light oscillator [33]

Lasers are generally classified based on different aspects such as (i) temporal properties (continuous wave or pulsed one), (ii) the lasing medium, and (iii) the laser wavelength. However, we have explained type of lasers based on temporal properties and lasing medium which are commonly accepted criteria to classify the lasers.

2.3.1. Classification Based on Temporal Properties

The output of laser can either be continuous wave (CW) or pulse wave, as shown in Figure 2.4. In CW mode, laser energy is delivered constantly for a long time. While in pulse wave, energy is rapidly delivered in a short duration

with high energy density. Generally, most of the gas lasers and some solid state lasers (Nd:YAG, semiconductor laser) are operating in CW mode.

In pulse mode, the repetition rate is the key issue. For generating the pulse lasers, various ways have been developed as follow:

- (1) Normal pulsing,
- (2) Q-switched, and
- (3) Mode locking.

Figure 2.4 Temporal mode of laser operation: (a) continuous wave mode, and (b) pulse mode

In normal pulse operation, changing the flashlamp parameters is mainly used to control the pulse duration. This is generally obtained by varying the inductance and capacitance of the flashlamp circuit. Figure 2.5 shows typical flashlamp circuit for producing the normal pulse.

In this mode, the laser system is operating at its natural rate and properties. Typical pulse duration for the normal pulses is of the order of microseconds to milliseconds.

Figure 2.5 Typical flashlamp circuit for laser pumping system [36]

Another technique is Q-switching. In this mode, the laser output can be modified by varying the properties of the resonant cavity. Short and intense laser output is generated by changing Q value of the cavity. Q value is the capability of the cavity to store the radiation energy. At the low Q values, the stored energy will be released as short and intense laser output. Thus, Q switching is a method of producing energetic short (but not ultrashort) pulses by modulating Q factor.

The Q-switching techniques can be summarized as: (1) rotating mirror method, (2) electro-optic method, (3) acousto-optic method, and (4) passive Q-switching. The pulse duration and the pulse repetition rate in this mode are generally in the range of nanosecond and a few hundred kHz, respectively [37].

Recent method for generating the laser pulses is the mode locking. In this mode, a periodic train of extremely short (ultrashort, typically sub-picoseconds) pulses is emitted. Interference between the longitudinal modes of the resonant cavity results in the mode locking (fixed phase) and then generates the oscillatory output. Modulating the loss or gain of the laser cavity at a frequency equal to the intermode frequency separation ($\Delta\nu = c/2d$), (c , speed of light, and d , resonator length) can lead to the mode locking (phase locking).

2.3.2. Classification Based on Lasing Medium

Types of lasers based on physical nature of the lasing medium can be also classified as follows:

- (1) Solid-state lasers,
- (2) Gas lasers,
- (3) Semiconductor lasers,
- (4) Liquid lasers, and
- (5) Free-electron lasers or X-ray lasers.

Although the lasing action has been shown in hundreds of materials, only a limited range of materials are being used to generate lasers commercially. Here, we will briefly explain the most used lasers in industry, solid state, gas and semiconductor lasers. Table 2.1 provides more important ones from each of mentioned categories.

Solid state lasers are lasers based on solid state lasing medium such as crystals, glasses which are doped with a small percentage of impurity ions (rare earth or transition metal ions). Although semiconductor lasers are in solid state, they are considered in semiconductor lasers category.

As shown in Table 2.1, there is large number of lasers available in solid state laser class. Among these, Nd:YAG laser is widely used in the laser material processing. Therefore, operating principles of this laser is described here.

Table 2.1 Typical types of lasers with their lasing wavelength [36].

Laser type					
Solid state lasers		Gas lasers		Semiconductors	
	λ (nm)		λ (nm)		λ (nm)
Nd:YAG	1,064	HeNe	632.8	InGaAs	980
Ruby	694	Argon	488,	AlGaInP	630-680
Nd:glass	1,062	Krypton	514.5	InGaAsP	1,150-1,650
Alexandrite	600-820	CO ₂	520-676	AlGaAs	780-880
Ti-sapphire	700-	ArF	10,600		
Er:YAG	1,100	KrF	193		
Nd:YLF	2,940	XeCl	249		
	1,047		308		

Nd:YAG laser are based on YAG crystals as a host material doped with neodymium ions (Nd^{+3}), with maximum doping level of 2%. YAG is the acronym for yttrium aluminum garnet with a chemical formula of $\text{Y}_3\text{Al}_5\text{O}_{12}$. Nd^{+3} :YAG is a four level lasing medium which is producing considerable gain even with moderate amount of pumping energy. Four-level energy laser system of Nd:YAG laser is shown in Figure 2.6.

This system has four discrete energy levels, pump level (E_3), upper-lasing level (E_2), lower-lasing level (E_1), and ground state (E_0). In a four-level laser, laser gain is realized as soon as pumping energy is applied to the system. Energy injected into the gain medium excites atoms to a pump level above the upper-lasing level. From there the excited atoms decay to the upper-lasing level and this usually occurs by emitting heat, not photons. It quickly populates the upper-lasing level which often has a longer lifetime than the lower level (and in most four-level lasers it does). So a healthy population of atoms builds in that level.

Lasing transitions now occur between the upper and lower lasing levels, emitting laser light in the process. There may not be a usable output beam since

any small gain produced will be lost to absorption and other losses within the system until threshold is reached. There is a population inversion and hence a gain. Injecting a little more energy into the system will raise the gain to a level where it exceeds lasing threshold and a usable output beam appears.

Atoms making a laser transition to the lower-lasing level decay further to the ground state. So the nature of a four-level laser is such that a population inversion is easy to achieve.

Figure 2.6 Four-level energy system for Nd:YAG lasers

Although 946, 1123, 1319 nm are emitted in Nd:YAG laser, but 1064 nm is the most common and strongest emission line in this laser. The output of Nd:YAG laser can be CW, or pulsed mode. With principle line emission of 1064 nm, laser outputs at 532, 355, 266 nm can be provided by the technique of frequency doubling, frequency tripling, and frequency quadrupling, respectively.

Gas lasers are the kind of lasers with a gas (or plasma) as gain medium. The gain entities are either single atoms or molecules which are often used in combination with other substances with auxiliary functionality. Gas lasers have significant advantages over solid state laser which are listed as:

- (1) Homogeneity of active medium,
- (2) Easy to transfer heat from the cavity and replenishment,
- (3) Relatively inexpensive active medium, and

- (4) Almost impossible to damage the active medium.

However, due to their low density, a high volume of gas is required to obtain the significant population inversion for lasing. Thus, the size of gas lasers is generally larger than that of solid state lasers. Gas lasers can be grouped according to their gain medium species:

- (1) Atomic gas lasers with the laser transitions between atom energy levels such as HeNe lasers and copper vapor lasers,
- (2) Ionic gas laser with the laser transitions between ion energy levels such as argon and krypton ion lasers, and
- (3) Molecular gas lasers with the laser transitions between molecule energy levels such as CO₂, CO, N₂, and excimer lasers.

CO₂ laser is one the most important gas lasers widely used for laser material processing, e.g. machining, cutting, welding and marking. Normally a mixture of CO₂, He, N₂, and possibly some H₂, water vapor, and/or Xe is used to generate a laser beam mostly at 10.6 μm as the most usual mode of operation. Addition of He provides high power output as well as removing the heat. H₂ and water vapor can also help to reoxidize CO (formed in the discharge) to CO₂. Both CW and pulsed modes can be achieved in CO₂ lasers.

Semiconductor lasers are using the semiconductor materials as gain medium. They are very small and very efficient, operating with relatively low pumping power. They have very widespread applications ranging from laser pointers to DVD players. Although semiconductor lasers may be initially considered as solid state lasers, they are actually very different in lasing phenomenon. The principle of semiconductor laser is based on recombination radiation.

When a p-type semiconductor is connected to the n-type semiconductor at a junction, the electrons under the attractive force from positively charged semiconductor start to penetrate toward p-type region. The holes from p-type region also begin to diffuse toward n-type region. The penetration of electrons and holes in opposite direction and resulting charge separation generates the

electric field at the junction. This electric field opposes the further charge diffusion of electrons and holes with the built-in potential barrier of eV_0 . When the external potential (V) is applied at the p-n junction such that the p-type region and n-type region are made positive and negative; this will cause reduction in the potential barrier from eV_0 to $e(V_0 - V)$. The reduction of potential barrier leads to penetration of electrons to p-type region and holes to n-type region. The recombination of electrons and holes leads to the spontaneous emission of photons, as shown in Figure 2.7.

Figure 2.7 Recombination of electrons and holes leading to emission of photons (so-called forward bias) [36]

Lasing action occurs when a certain threshold current is applied to generate enough population inversion at the junction and then stimulate emission of photons. Typical structure of homojunction semiconductor laser is shown in Figure 2.8. Homojunction lasers are composed of single semiconductor mainly GaAs. In such lasers, the concentration of electrons and holes at the p-n junction leads to higher refractive index at that region. This causes the internal reflection and confinement of the emitted light.

Figure 2.8 Schematic of a semiconductor laser [38]

2.4. Common Issues on Laser Processing of Materials

2.4.1. Effect of Wavelength

When the incident laser beam with the intensity of I_0 interacts with the material surface, different physical phenomena occurs at the interaction region including reflection, absorption, scattering, and transmission, as shown in Figure 2.9. Laser light for producing any obvious effect on the irradiated material must be first absorbed. Absorption, the interaction between the material electrons and electromagnetic radiation, depends on the wavelength of the incident beam and optical properties of the material [39]. Thus, it shows that absorption of laser beam by material is a very critical factor in laser processing.

Figure 2.9 Schematic diagram of interaction of incident laser beam with material

The reflectance of the material surface (R) determines the amount of reflected light ($R \cdot I_0$) at the surface. While the rest of incident light will be absorbed, scattered and transmitted through the material, as shown in Figure 2.9. The irradiance of absorbed light can be expressed by [40]:

$$I(z) = (1 - R)I_0 \exp(-\alpha z) \quad (2.8)$$

where, α (m^{-1}) is the absorption coefficient. The inverse of the absorption coefficient ($1/\alpha$) represents how far the light can penetrate in the material before getting absorbed completely. This distance is called optical penetration depth.

The absorption coefficient (α) is defined as:

$$\alpha = \frac{4\pi k}{\lambda} \quad (2.9)$$

where, k is the imaginary part of the refractive index of the material and sometimes called extinction coefficient. It is defining how strongly a material can absorb a light at a certain wavelength per unit mass. From Equation (2.9), it is implied that the shorter the wavelength the shallower the penetration depth is. The shallow penetration depth means the absorbed laser energy is concentrated in a small volume of material and therefore due to high density of energy it will lead to more effective ablation and material removing.

Generally, metals show the opaque behavior to the laser beam and therefore light can be absorbed effectively within very thin layer of material surface which is about 10nm. However, there are some typical metals like gold, aluminum, and copper, showing very high reflectance (near 1) to infrared (IR) lights. Thus, direct processing of these metals with Nd:YAG ($\lambda = 1.064 \mu\text{m}$) or CO₂ ($\lambda = 10.64 \mu\text{m}$) laser cannot be efficient with respect to the energy. In the case of silicon, near IR and even IR laser beams transmit in over hundred of micrometers without remarkable absorption. However, the absorption of ultraviolet (UV) light is very high and completely absorbed within about 10nm [40]. Therefore, proper selection of laser beam wavelength is very important in laser material processing.

2.4.2. Effect of Pulse Duration

Pulse duration of laser beam is also of vital importance in laser material processing from laser-matter interaction point of view. Figure 2.10 demonstrates CW laser, nanosecond, and pico/femtosecond laser pulses interactions with matter.

The CW laser interacts with matter in such a way that the thermal energy deposited by the laser diffuses away during interaction time. The laser-matter interaction time is longer than the heat diffusion time (in the range of few ns). Heat diffusion into surroundings creates large heat affected zone (HAZ) as shown in Figure 2.10(a). It also reduces the focal spot temperature and results in the working temperature not much above the melting point. Therefore, CW laser removes the material mainly by melting and partially by evaporation.

Figure 2.10 Laser-matter interaction in different pulse duration: (a) CW laser, (b) ns laser, and (c) ps/fs laser. HAZ: heat affected zone.

In ns laser-matter interaction, smaller HAZ is created due to shorter interaction time, as shown in Figure 2.10(b). Deposition of a lot of energy into the irradiated and melted point causes boiling, vaporizing, and sputtering of the melted materials. Therefore, material removing occurs mainly by melt ejection driven by the vapor and recoil pressure. The ejected melt falls back onto the substrate surface and contaminates it. On the other hand, the heating and cooling wave propagating through the HAZ can cause mechanical stress leading to microcracks in the surrounding materials. Furthermore, heat diffusion in long pulse-matter interaction can produce shock waves that cause damage to nearby structures especially in multilayer materials. The side effects associated to this regime are listed below and also can be seen in Figure 2.11.

- (1) surface ripples due to shock wave
- (2) damage caused to the adjacent structures
- (3) recast layer
- (4) surface debris

- (5) microcracks
- (6) larger heat affected zone
- (7) shock wave

Figure 2.11 Long pulse laser-matter interaction and the associated drawbacks [41]

Thus, these collateral effects that are mostly dominated by thermal diffusion are often limiting factors and undesirable in laser micromachining with long (about ms and μ s) and short (about ns) laser pulses.

Ultrashort (about ps or fs) pulses heat and ablate the material via direct vaporization and rapid formation of plasma. This causes almost negligible HAZ and shock wave damages, as shown in Figure 2.10(c). In this ultrashort laser-matter interaction regime, deposited laser energy does not have time to diffuse away from the irradiated area. The duration of the laser pulse (less than about 10 ps) is much shorter than the heat diffusion time.

Therefore, laser machining with ultrashort pulses offers more precise and clean material processing as shown in Figure 2.12, with almost none of side effects associated to long and short pulses.

Figure 2.12 Ultrashort pulse laser-matter interaction and with almost no side effects [41].

2.4.3. Diffraction Limit of Laser Beams

Laser material processing has gained many successful applications in various engineering fields including welding, cleaning, surface modification, micro/nano machining, etc. In most cases, diffractive behavior of the laser beams in the far field is one of the reasons to limit the feature size and resolution of laser-machining that is generally above $1\ \mu\text{m}$. Far field refers to cases where the distance of irradiated surface from optical lens is greater than the beam wavelength. Diffraction limit of the beam in the far field can be expressed by [42, 43]:

$$d = \frac{\lambda}{2n \sin \theta} \quad (2.10)$$

Where d is the spot size, λ is the beam wavelength, n is the refractive index of the irradiated medium and 2θ is the angle through which light is collected by an optical instrument. θ is also called diverging angle of the beam. Theoretically the best resolution that can be achieved is around $\lambda/2$. The laser wavelengths in many engineering fields are in the range of 248 nm - 10.6 μ m. So, direct laser surface texturing in nano scale (≤ 100 nm) resolution has remarkable challenges.

To overcome the diffraction limits of the laser beam and nano scale laser surface texturing, some approaches have been suggested such as optics with high numerical aperture, shorter wavelength lasers, near field optics, and femtosecond pulsed lasers.

For instance, deep ultraviolet (DUV, ArF 193 nm) lasers have been utilized to fabricate stripes of 130 nm and 90 nm lithography [42]. Furthermore, to pattern smaller surface features, F₂ lasers ($\lambda = 157$ nm) and extreme ultraviolet (EUV) lasers (5 to 50 nm) have been used for nano lithography. But, EUV systems are expensive, low power, and unstable in high intensities. Thus, because of the high absorption of UV laser in air, the nano lithography needs to be done in a vacuum or pure N₂ environment. N₂ atmosphere has often been selected for its very high bond energy (≈ 9.8 eV). Therefore, the usage of more stable light sources (UV, visible and IR lasers) has been globally gaining high research attentions in order to solve the optical diffraction limits.

Near field optics is the technique to pattern features beyond the diffraction limits. It is using the evanescent waves at the distance that is in the range of the beam wavelength.

Also femtosecond pulsed lasers due to the ablation threshold setting and nonlinear absorption effects have been successfully used to obtain nano scale production in far field.

2.5. Laser Direct Writing of Micro/Nano Structures

2.5.1. Nanosecond (ns) Laser Direct Writing

Laser direct writing of micro and nano structures is rapidly widening due to the ability to modify a variety of materials at small feature sizes within short processing time. Nanosecond lasers as one of the processing and manufacturing tools has gained more attraction in extended applications in modern microelectronic industries, surface modifications, marking, drilling, and annealing [44, 45] and also in medical devices like stents [46].

Brief review of ablation mechanism in ns laser direct writing would increase our understanding of this very important micro/nano manufacturing tool. Laser direct writing with ns laser that is based on ablation has been analyzed on the basis of thermal, mechanical, photophysical, photochemical, and defect models [44]. Based on a particular material and laser parameters, each of these models could be dominant to describe ablation. However, a more general description needs simultaneous consideration of the different interaction mechanism and their coupling.

Figure 2.13 represents the different interaction and feedback mechanisms involved in pulsed laser direct writing (ablation). The ablation process begins with laser light absorption and then material excitation. The photon energy and optical response of the material determine the dominant ablation mechanism.

If the photon energy or optical absorption coefficient of the material is low, laser beam energy will transform into heat and result in the temperature rise. The temperature rise can lead to thermal material ablation (vaporization) with or without surface melting. It can also induce stresses (creating explosive-type ablation) and defects that both could be influencing factors in thermal ablation.

If the photon energy is high enough, laser-induced excitation can lead to direct bond breaking, and adsorption of single atoms, molecules, and clusters. It can also create defects (photochemically dissociated bonds) that build up stresses and eventually (mechanical) ablation. This type of ablation generally

occurs with very low change in surface temperature so that it is called photochemical ablation or sometimes cold ablation.

Photophysical ablation describes a process in which both thermal and photochemical (non-thermal) mechanisms have contribution to the overall ablation rate. It is believed that photophysical ablation mechanism may dominate the ablation process in ns laser direct writing.

Figure 2.13 Different interaction and feedback mechanisms involved in pulsed laser ablation. Thermal-based ablation (left path), direct bound breaking (photochemical ablation or cold ablation; right path), or photophysical ablation (combination of thermal and photochemical ablation; intermediate path) [44].

After a brief review on the ablation mechanism, we have reviewed some of the applications of ns laser direct writing.

Surface structuring of some non-absorbing materials has been conducted using coating mediated ns-ablation. For instance, ablation of non-absorbing fused silica with ArF ns laser is conducted using a solid coating (SiO) as an

absorbent of the laser radiation [47]. Plasma formation results in material removal from non-absorbing silica.

F₂-laser ablation was used to pattern of piezoelectric gallium orthophosphate (GaPO₄) crystals (with very high bandgap energy 7.1 eV) that is employed for gas sensing [48, 49]. Structuring of ceramics PZT with XeCl excimer radiation was also reported by Eyett et al [50].

Fabrication of microholes, grooves, gratings using ns laser ablation was widely investigated for usage in sensors, microfluidic devices, optoelectronic devices, solar cells, etc. For instance, formation of high quality periodic surface grating, graded transmission dielectric masks, metal foil and thin mask were reported in [51, 52]. Also, microstructuring of thin films used in solar cells and nanotechnology were studied in [53-56].

2.5.2. Femtosecond (fs) Laser Direct Writing

Direct writing of micro or nano scale features using fs laser is different from other methods of conventional laser direct writing. This is mainly due to its nonlinear interaction mechanism with matter. In fs laser-matter interaction, the interaction time ($10^{-15} - 10^{-13}$ s) is shorter than the electron-lattice relaxation time (10^{-11} s or 10 picoseconds). Therefore, the deposited laser energy cannot diffuse away from electrons to the lattice and the material stays cool during the laser absorption. Due to the very short interaction time of fs laser pulses, it limits the thermal diffusion, decreases surface roughness and the thermally affected zone as mentioned before and shown in Figure 2.12. Therefore, the above mentioned advantages make fs laser to be suitable tool to write couplers [57], waveguide amplifiers [58], diffraction grating and memory bits [59]. Fs lasers have been recently used to improve precision of medical devices like stent [60].

Even far field production beyond diffraction limit is achievable by fs laser writing. This would be possible when only the peak of gaussian beam is above the threshold of ablation or phase change in the material.

The essential thing in fs laser micro and especially nano fabrication is precisely focusing the light using a high numerical aperture (NA) telecentric lens. Using such lens causes the normal incidence of the beam over the target surface and then fabrication of even features. Less fluctuation in laser energy and accurate scanning system ensure the fabrication with high precision. Optical tuning and the fabrication vision are conducted using the charge-coupled device (CCD) camera [61].

Critical factors in fs laser processing arise due to nonlinearity in the material properties (chemical and optical) during laser-matter interactions [42]. When the sample surface is irradiated with fs laser, the absorption of photons could be occurred by one photon, two photons, or multi photon absorption. The absorption causes different process including electron excitation, ionization and phase changes. The electrons are excited and vibrated by the absorbed energy and their kinetic energy is transferred into thermal energy by collisions with ions through inverse Bremsstrahlung mechanism. Such phenomena can only happen at the focus spot due to very high intensity. The energetic electrons with energy exceeding the binding energy escape the target surface and create a strong electric field of charge separation with the parent ions. This causes a high electrostatic field close to the surface and leads to pull out the materials (ions) in a non-equilibrium process called electrostatic ablation or Coulomb explosion. This is also the reason that the fs laser processing is so called cold laser processing that makes the writing of transparent material possible [62-64]. In conclusion, the formation of nano features depends on the interaction between the fs laser, the fs-induced electron plasma and the material [65]. Two-photon absorption mechanism are shown in Figure 2.14 [66]. S_0 , S_1 , and S_2 are ground state, one-photon and two-photon excited states, respectively. The frequencies of incident light are ω_1 , and ω_2 while the fluorescent emission frequency is ω_3 .

Figure 2.14 Illustration of energy levels in two-photon absorption process [66].

Generally, the materials in standard optical lithography excite to the first order. For two-photon and multi-photon absorption in fs laser nano-writing, the response is restricted to two or higher number of absorption levels. This is the reason why the photon energy in two-photon absorption is lower than that in one-photon absorption. Thus, the irradiated volume in fs laser-matter interaction decreases and this results in smaller irradiated region and improved resolution in surface structuring. The volume of absorbed energy is less than λ^3 , thus this improve the resolution of the structuring process beyond the diffraction limit (≤ 100 nm) [67].

It is necessary for nanoscale writing that the deposited laser energy goes through the material without any considerable losses. Because of this reason, a laser from near infrared region (800 nm for instance) is chosen for nano writing. Due to their high intensity, fs lasers can excite and ablate various materials.

Femtosecond laser processing has many advantages over the longer pulsed laser processing, which make them to be used for nano-structuring of various materials such as metals, polymers, ceramics, and semiconductors. [68-70]. Examples of the nano features (≤ 100 nm) written by fs lasers are shown in Figure 2.15.

Figure 2.15 Nanofeatures developed in (a) amorphous silica [71], (b) urethane acrylate resin [67], (c) commercial resin, SCR 500 [72], (d) glass [73], (e) TeO₂ [74], (f) photoresist thin film [75], (g) CVD diamond surface [76].

2.5.3. Micro Lens Array for Fabricating Periodic Nano Structures

Periodic nano-structures are highly required for plasmonic structures, photonic crystals, data storage, and optical grating. Micro lens array (MLA) lithography is a laser based method which is mainly developed for rapid periodic nano structuring of large scale area. MLA includes a series of same and small lenses which are typically configured hexagonally or squarely packed. During illumination, MLA can focus a laser beam to many light spots on the focal surface.

Optical performance of a lens could be improved by lowering the diameter, D , and the focal length, f [77]. In case of a constant F number $F=f/D$, the diffraction limited resolution is given by $\delta x \approx \lambda F^2$ which is not dependent on the lens size. However, it should be considered that a smaller lens causes less wave aberration for the same F number and wavelength. The wave aberration is described as the deviation of the actual wave front from a perfect spherical wave front [78].

The early investigation on using micro-lens arrays for photolithography can be found in [78, 79] with the application to the manufacturing of periodic micro features. With improving the technology of micro-lens array fabrication, the micro lenses' size becomes smaller and makes the size of written features even smaller. For example, many of the field emission transistor structures in short time with a gate line width of 200 nm have been fabricated on a 30 nm-thick GeSbTe layer using an 800 nm wavelength and 100 fs pulse width [80]. Furthermore, laser irradiated samples were etched by alkaline solution and nanostructures down to 50 nm on thin films were produced [81]. To achieve more smaller feature sizes, they fabricated a micro-lens array on a quartz surface with diameter 1 μm and pitch 1 μm that is composed of 2500×2500 (6.25 million) lens covering an area of 5 mm $\times$ 5 mm. The fabricated MLA was used to irradiate UV light-sensitive photoresist using a 248 nm wavelength, 23 ns pulse width KrF excimer laser. This led to fabrication of nano-dots as small as 78 nm in diameter, at a resolution of $\lambda/3$ [80]. Figure 2.16 shows an example of periodic features fabricated by a micro-lens array system.

Figure 2.16 Large area micro-nano structures fabricated by laser MLA [80]

The technical challenge in MLA is to locate the lens horizontally to the target surface during the radiation to guarantee that the laser is vertical to the target surface. It is also important to adjust precisely the distance between the lens and the target surface.

Therefore for non flat surfaces, it is quite challenging to produce uniform features using micro lens array technique.

2.6. Laser Direct Writing beyond Diffraction Limit (Near Field Techniques)

2.6.1. Laser Coupled Near Field Scanning Optical Microscopy (NSOM)

Laser coupled NSOM is a technique for laser direct writing beyond diffraction limit using laser beam (e.g. a frequency doubled argon ion laser at 244 nm wavelength) with an optical fiber based NSOM (first demonstrated in 1992). The method is generally used in scanning near field photolithography (SNP). Optical fiber with a very fine tip (typically $D = 50$ nm) is located very close (10 – 20 nm) to the target surface. Evanescent energy field with a high resolution (beyond diffraction limit) is generated at the optical fiber tip. This energy field is highly dependent on the distance between the tip and target surface and decays rapidly with distance. The distance should be hold in nanometer range to ensure the arrival of the enough energy density to the target surface.

The structured photo-resist is further processed by chemical etching, plasma etching or UV radiation to produce nano scale features on the target surface. Lo and Wang for the first time in 2001 reported the fabrication of narrow grooves (128 nm FWHM) by an optical fiber probe with Ar^+ laser (488 nm) [82]. The results showed the near field lithography's superiority because the linewidth is smaller than one-third wavelength (162.7 nm). Sun and Legget [83, 84] reported selectively oxidizing a strongly bound self-assembled nanolayer photo resist on a gold substrate by scanning near field photolithography that is followed by chemical etching to realize 20 – 55 nm in surface structuring. The resolution obtained by this method is matching that of

electron beam lithography but without the need of vacuum chamber that is very costly.

Further development of this technique was conducted by Lin et al [75, 85], Chong et al [86]. They have used a frequency-doubled Ti:Sapphire femtosecond laser with 400 nm wavelength which is coupled into an NSOM fiber probe to achieve 20 nm resolution surface structuring on a UV photo resist spin coated on a silicon for data storage applications. In this study, the shear-force feedback system based on tuning-fork mechanism was used to adjust the tip-sample distance.

As mentioned before, the critical parameter in the coupled laser and NSOM nano fabrication technique is the distance between probe and sample which is controlling the size and shape of nano features. The NSOM with a small probe diameter and probe-to-sample distance can be used to overcome the traditional far-field diffraction limits and to get sub-wavelength structures. Figure 2.17 shows an example of nano-line arrays produced at various laser powers. In addition, width and depth of lines can be adjusted by the writing speed so that higher writing speed results in shorter exposure time then a narrower line width and shallower depth.

The NSOM tip with metal coating has a melting threshold, generally low power (<1 mW) laser needs to be used in this technique to avoid damaging of the tip. The drawbacks of the method include the need for precise controlling of nano distance between tip and sample, and potential contamination or damage to the fiber tip. In case of dealing with rough surfaces (> 50 nm R_z), the application of the method is limited.

Alok et al [13] have reported a recent developed technique to enable nanosecond laser NSOM method with 200 nm probe diameter which is applied to fabricate nano features directly on silicon with no need of subsequent etching processes.

Figure 2.17 Nano-lines produced by the femtosecond laser/NSOM SNP method at various laser powers [85].

2.6.2. Contact Particle Lens Array (CPLA) Nano Fabrication

CPLA is a recently developed technique based on using transparent micro spheres that are distributed on the substrate by self-assembly to create a monolayer of spheres. The micro sphere performs as a micro lens and enhances laser intensity at the contact point of the particle and the substrate. This is suitable for high resolution patterning. The intensity can be increased up to 50 times for a 266 nm and a 500 nm particle, [42]. Intensity enhancement increases with increasing the particle size and decreasing the wavelength. However, increasing the particles size leads to a larger area of energy field concentration hence decreased resolution. In addition, there is also a limit on laser wavelength because of the nature of the particle materials. For example, the absorption of the most optical materials and even air is very high for a F_2 excimer laser with $\lambda = 157$ nm. Thus, in order to get the smaller region of enhanced light, a small particle size should be chosen. This technique is applicable for surface nano structuring on various materials directly with no need of lithographic methods.

The phenomena of light induced surface damage through micro and nano particles were known in late 1900s in the process of laser surface cleaning. Kawata et al [87] used the phenomenon for high resolution optical microscopy. They have produced topological changes on a polymer surface using very small (50 – 100 nm) optically transparent sphere [87]. Lu et al studied the use of microspheres as a tool for laser nano patterning of silicon substrate [88]. They used 0.5 μm silica spheres irradiated by a 248 nm excimer laser to fabricate 100 nm protrusions on silicon.

Using of polystyrene sphere for laser nano patterning on large area has been reported by Hasegawa et al [89]. Self-organized hexagonally closed packed monolayer of polystyrene spheres was irradiated using Ar^+ laser (488 nm) to fabricate 95 nm structures on polymer surface.

Münzer et al. [90] have reported the generation of nano holes (diameter < 100 nm, and depth < 10 nm) on glass and silicon using polystyrene microspheres irradiated with a laser beam. By applying Mei theory, they have calculated the near field intensity enhancement of an irradiating beam with $\lambda = 800$ nm. They found that the incident field is not focused at a distance of

$$f = r \frac{2-n}{2(n-1)} \quad (2.11)$$

from the particle surface as expected from geometrical optics , but the maximum field intensity is in this example right at the surface of the particle. n is the refractive index of the sphere and r is the radius of the sphere. When the sphere size is below the incident wavelength, two focusing peaks were found that led to the double spots generated on the substrate surface. For practical applications, the microsphere diameter is normally greater than the incident laser wavelength.

Figure 2.18 demonstrates an example of hole arrays fabricated on $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) / Al thin film using the CPLA method that is conducted by Li

et al [42]. Closely packed colloidal monolayer of 1 μm polystyrene microspheres were used and irradiated by a KrF excimer laser at the fluence of 5.8 mJ/cm^2 . Bowl shaped nano holes were produced with uniform diameter.

Figure 2.18 SEM image of nano hole arrays formed on a GST thin film surface after one pulse of KrF excimer laser irradiation at a laser fluence of 5.8 mJ/cm^2 [42].

The focal length of micro spheres can be changed using a different medium between spheres and substrates such as water or chemical solutions [91, 92]. Therefore, sub-surface patterning and swelled patterning such as surface nano bumping on silicon has been reported. Moving a laser over the particle lens makes the fabrication of non-periodic nano patterns possible [93].

Although microsphere near field nanostructuring is reliable and allows the large scale structuring, its flexibility of feature geometries has been limited to holes or pits. The limitation of CPLA method has been solved by new approach proposed by Guo and Li et al [56, 94, 95] using an angular scanning particle lens array. The technique resulted in producing periodic lines, curves, and arbitrary patterns. Figure 2.19 shows the a typical process configuration in the angular scanning particle lens array method. Figure 2.20(a) shows an example of the complex patterns produced using the technique without using any mask.

Figure 2.20(b) represents the enlarged view of single nano star that was fabricated in several million quantities on a $1\text{ cm} \times 1\text{ cm}$ surface area [95].

The disadvantage of the method is that the produced patterns are not perfectly uniform. This is because of the intensity varying at each point and the existence of multi layer particles at some points.

Figure 2.19 Illustration of angular scanning particle lens array method for nano fabrication [56]

Figure 2.20 Nano star array (a) a section of $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ and (b) a single nano star from the array [95].

To solve the problems of non-monolayer particles and on curved or hydrophobic surfaces, a particle lens transport system has been recently developed by Ashfaq et al [96]. The method allows the reuse of the particles and also for patterning on curved or hydrophobic surfaces. In the proposed technique, a hexagonal closed packed monolayer of SiO_2 spheres is first formed by self-assembly on a flat glass surface. The formed monolayer of particles is then picked up by a flexible optically transparent sticky surface and placed on the substrate to be patterned. The method is shown in Figure 2.21. It has been applied successfully for nanopatterning on a Ti tube and on a hydrophobic silicon surface without pre-treatments.

Application of metallic nano particles (e.g. Ag, Au) has been also studied in order to create smaller nano-features through plasmon enhanced near field effects [97-99].

Figure 2.21 A schematic illustration of the particles transfer method, (a) monolayer formed on the surface of glass, (b) ribbon is placed on monolayer and pressed, (c) ribbon is lifted from glass surface along with monolayer, and (d) ribbon is wrapped around the Ti tube [96].

2.6.3. Micro-sphere Assisted Nano Writing Based on Optical Tweezers

Optical tweezers use light to control microscopic objects as small as a single atom. The radiation pressure at the focus point of laser beam is able to trap small particles. Figure 2.22 shows more details at how the optical tweezers work. The basic working principle of optical tweezers is the momentum transfer associated with bending light. Light momentum is proportional to its energy and in the propagation direction. Any change in the direction of light (e.g. by reflection or refraction) will lead to a change of the light momentum. Thus, if an object bends the light, this will change its momentum. Based on the conservation of momentum, the object must experience the same value but opposite momentum change. This will cause forces acting on the object and trap it into the light propagation direction [100], as shown in Figure 2.22.

Figure 2.22 optical tweezers principles.

Laser nanostructuring based on laser tweezers has been recently developed by McLeod and Arnold [101]. In this method, a transparent sphere

(polystyrene) was held using a focused continuous wave laser beam (as trapping tool). This trapping laser beam is transferred to a Bessel beam by an axicon lens as in a typical laser tweezers setup in a liquid environment. Another laser beam ($\lambda = 355 \text{ nm}$, $\tau = 15 \text{ ns}$, $E = 15 \text{ nJ} - 8 \text{ mJ}$) as a processing laser at the same time with trapping laser beam illuminates the sphere and produces a focused and enhanced (based on near field effect) energy at the contact spot area of the sphere and sample. Thus by moving the sphere over the substrate surface, nano scale features have been patterned. Advantage of the technique is to maintain constant distance between the sphere and sample surface even for the curved surface without any additional feedback system. This is due to the balance between the radiation pressure of laser beam and the electrostatic repulsion from the ionized target surface [102]. Figure 2.23 shows a typical optical tweezers setup and an example of a nano pattern produced using the technique.

Figure 2.23 (a) Schematic of the experimental setup, depicting the paths of the trapping laser (green, 532 nm) and the processing pulsed laser (purple, 355 nm). The white light is used in conjunction with the $\times 50$ objective and CCD camera to monitor the process. (b) An example of optically trapped micro-sphere nano writing. The scale bars on the larger picture and the zoomed one are 2 μm and 250 nm, respectively [101].

For large area nano patterning, McLeod and Arnold [101] have developed the technique by dividing the trapping beam into the multiple beams using beam splitters to hold and move several microsphere ($0.76 - 3 \mu\text{m}$ diameter) over sample surface. Using such system enables them to write a number of nano patterns on a polyimide film coated on a glass substrate. An advantage of the technique comparing with other near field direct writing is that it does not need expensive high precision distance controller and also it can work on rough surface [103]. A drawback of the technique is the requirement for a liquid processing environment.

2.7. Laser Induced Periodic Surface Structures

Laser induced periodic surface structures (LIPSS) or so-called ripples have been observed frequently in laser surface processing, as shown in Figure 2.24 [104]. Ripples formation on an irradiated surface was first observed in 1965 by Birnbaum [105] after the demonstration of the first laser (Ruby laser). LIPSS formation consists of the development of wavy surfaces that comes due to the interference of the incident and reflected/refracted laser light with the scattered (diffracted) light from the surface. Scattering of the incident light can be caused by irregularities in the propagation medium (e.g. defects or spatial variation in the dielectric constant), particles, and surface roughnesses.

LIPSS have be fabricated in variety of materials with the period depends on the wavelength ($\Lambda \propto \lambda$), the angle of incidence (θ_i), the polarization of laser beam, the laser fluence.

Figure 2.24 Image of the ripples produced on Ge with linearly polarized 1.06 μm Nd:YAG laser radiation at perpendicular incident [104].

The orientation of ripples is usually determined by the polarization of the incident laser beam and in some cases by θ_i . With metals and semiconductors, linearly polarized laser results in the formation of ripples oriented perpendicular to the electric field vector of the incident light [44]. With dielectrics, ripples with both perpendicular and parallel orientation were observed. In case of circular polarization, the ripples with no specific orientation were observed [42].

Laser processing with intensity below the ablation threshold can lead to regular surface structures in nano scale. Nanometer kerfs in synthetic single-crystal CVD diamond have been fabricated with femtosecond pulses [106]. Grooves are vertical to the polarization direction and are 40 nm wide, 500 nm deep, and have an average spacing of 146 ± 7 nm. Ripples initially have been considered only as laser induced surface damage of optical components. However, in recent years it has been realized that the rippled surfaces have very interesting properties and large surface area can be structured by overlapping short laser pulses. Ripples are generated when certain laser densities are deposited on material surface. Outside of this range, other surface features are produced. For example, below the threshold fluence for the ripples formation on metals, small spheres are produced. These spheres or some time called bubbles

have diameter in the range of 10 -90 nm. When the deposited energy is increased, for instance, by applying lower processing speed, the periodic patterns turns into more irregular structures [107]. The height of ripples is in nanometer scale ranging from 10 nm to value above 100 nm [108]. Nano rippling of large area can be conducted by aligning the ripples between each laser scanning tracks [109].

Ripples formation on the irradiated surface are reported on a variety of materials. Most studies on the ripples formation are conducted for metals and semiconductors as well as dielectrics such as glass, diamond, and ceramics. Even polymers show periodic patterns. Nanosecond lasers in 1970s and 1980s were used for the ripples formation. However, picosecond and femtosecond lasers in 1990s and the first decade of this century become available for micro/nano ripple formation. Figure 2.25 shows nano scale ripples formed on alloy steel with fs laser radiation. Nano sized bubbles with diameters in the range of 20 - 100 nm were found on top of the fine ripples.

Figure 2.25 Scanning helium ion microscopy (SHIM) image of fine ripples with lateral sizes of 172 nm oriented parallel to the polarization direction formed with fs laser pulses on alloyed steel [108].

Although LIPPS have already been observed for more than 45 years, the formation mechanisms are still under discussion. However, two kinds of formation mechanisms have been summarized in literature.

- (1) The resonant mechanisms: these mechanisms are based on electromagnetic aspects, as inhomogeneous energy absorption just beneath the surface due to the surface roughness, as plasmon excitation on surface [110]. This is the most commonly accepted explanation for the ripple formation mechanism. If we put it in simple words, the ripples formation could be described as a result of the interference of the incident and reflected or refracted laser light with the scattered or diffracted light near the interface.
- (2) The non-resonant mechanisms: these mechanisms are more attributed to the thermal or chemical results of the laser irradiation of the target surface, like thermocapillary waves or chemicapillary waves acting as driving force on the melted layer [111].

The intensity of the scattered wave depends on the irradiation parameters and the electromagnetic response of the material. If the material has an optically active mode near the incident light frequency, it is assumed that the scattered light can directly excite a real surface electromagnetic wave (SEW) [112]. Such SEWs or surface polaritons are waves travelling along the interface between two media.

If there is no optically active mode near the incident light frequency, ripples are supposed to form when one of the diffracted waves propagates close to the surface.

2.8. Laser Induced Plumes

Irradiation of a material surface with a high intensity laser beam would eject the material particles from the surface and form a cloud of ablated material that is expanding rapidly from the surface. Such a cloud of ablated material is

called laser induced plume that is composed of neutrals (excited or ground-state), ions, electrons, and clusters.

Laser induced plume as a strongly light emitting cloud is growing in all directions, but preferentially along the target normal. An example of the plume expansion is shown in Figure 2.26. It has transient nature with characteristic parameters that develop quickly and are highly dependent on irradiation conditions such as laser intensity, laser wavelength, irradiation spot size, laser pulse duration, ambient gas composition, and ambient pressure [113, 114].

The physical parameters in the plume (e.g. mass distribution, electron/ion density, ion/atoms velocity, and angular distribution of the plume species) are of crucial importance in laser ablation applications such as mass analysis, analytical sampling [115, 116] and production of thin films by pulsed laser deposition (PLD) [113, 117, 118]. In particular, the shape of plume that is expanding from the target surface to the substrate determines the thickness distribution of deposited thin film [119, 120].

Figure 2.26 Image of the LaMnO_3 plume at two background gas pressures, P , and at different time delays τ after the onset of plasma formation using XeF excimer laser pulses (duration = 20 ns (FWHM), $\lambda = 351$ nm) and fluence of 1.5 J/cm^2 . $P = 0.3$ Pa at (a) $\tau = 0.9 \mu\text{s}$, and (b) $\tau = 3 \mu\text{s}$; $P = 9$ Pa at (c) $\tau = 0.9 \mu\text{s}$, (d) $\tau = 3 \mu\text{s}$ and (e) $\tau = 7.5 \mu\text{s}$. The upper right illustration shows the experimental setup used for the time-resolved imaging analysis by fast photography technique [121].

Different complicated interaction mechanisms are involved in laser ablation process including laser absorption, evaporation, transient gas dynamics, radiation transport, condensation, ionization, and recombination. A detailed theoretical or computational treatment has not yet been developed for the relatively simple case of a plume expansion in vacuum. Laser ablation process in PLD with gas background is considered as a very complex case.

Therefore, any optimization of laser ablation-based processes particularly the film deposition in PLD requires the comprehensive understanding of the plume dynamics.

Several techniques have been developed to characterize the complex physics of expanding plume. They include optical emission spectroscopy [122, 123], mass spectroscopy [124], Langmuir probe [125], microwave and laser interferometry [126, 127], Thomson scattering [128] and etc. Fast photography is also another method to study the laser induced plume providing two dimensional snap shots of 3D plume propagation [129, 130]. This method becomes highly required to understand the hydrodynamics of the plume propagation.

Laser ablation process and laser-induced plume propagation can be considered as a set of complicated phenomena during which several basic steps occur. The whole picture of plume formation process is summarized and shown in Figure 2.27.

The process is initiated when the laser beam strikes the solid surface. Some part of laser beam is reflected at the solid surface and the remaining part is absorbed by the electrons in the solid as shown in Figure 2.27(a). After a period of tens of ps, the absorbed energy is transferred from electrons to the lattice (atoms) that results in a strong heating of irradiated volume. In this stage, laser-matter interaction dominates the phenomenon.

At the moderate laser intensity ($\approx 10^6 \text{ W cm}^{-2}$), the absorbed energy is rapidly turned into heat that leads to melting and sample vaporization, as shown in Figure 2.27(b). This explanation can be thought to be the case in lasers with pulses of ns or longer duration. For ultrashort pulses (fs lasers), pulse period is too short for any lattice (atomic) disordering to occur when the pulse ends.

The vapor, including submicrometer sized droplets as seen in Figure 2.27(b), continues to absorb energy from the laser, resulting in the strong heating and ionization of vapor and eventually the formation of ionized vapor/plasma on the target surface, as shown in Figure 2.27(c). In this stage,

laser-gas or laser-plasma interactions are dominant with several complex processes happening both in the solid and in the ablated matter.

When the laser pulse terminates, photoablated fragments of the plume expands adiabatically in three dimensions [131], as shown in Figure 2.27(d). In case of plume expansion in vacuum, the shape and velocity distribution in the plume will eventually reach constant value [131]. However, if the ablation process happens in a background gas, the high pressure of plume initially drives the expansion the same trend as of in vacuum. After few μs , the plumes dynamics is totally determined by the interaction of the plume with the background gas.

Figure 2.27 Illustration of the different processes involved in laser-matter interaction and ablation, (a) light reflection and absorption in the solid, (b)

heating, melting, evaporation and the removal of matter from surface, (c) absorption and scattering of laser beam by vapor leading to ionization and plasma formation, (d) fast expansion of laser plume (photoablated fragments), (e) subsequent cooling of matter, formation of polyatomic aggregates and clusters, and (f) ablated material deposition.

Subsequent cooling leads to the formation of polyatomic aggregates and clusters as shown in Figure 2.27(e). After a particular period of time, the ablated materials together with the melted materials are deposited on the target surface around the crater, as shown in Figure 2.27(f). The shape and size of the deposited materials depend on the material properties and irradiation parameters (fluence, wavelength, pulse width).

The expanding plume is heated by different absorption mechanisms that attenuate the laser beam energy transmitted to the solid/liquid interface. This absorption provides the kinetic energy for the expansion [132].

2.9. Magnetic field assisted laser welding and hardening

The use of a magnetic field in laser material processing is of great interest since a magnetic field can be used to effectively control the dynamic properties of laser produced plasma (LPP). Besides its basic research importance, the effect of a magnetic field on the expansion dynamics of LPP has also gained importance in applied research such as pulsed laser deposition (PLD) techniques, magnetic field assisted laser welding and hardening.

Before getting into the magnetic field assisted laser welding and hardening, we have briefly reviewed the techniques which have been used to control the laser-induced plasma during welding process.

The Plasma cloud produced during high-power laser welding has always been an interesting topic to explore. The problems associated with this plasma are manifold. Firstly, when its ion/electron density is below the Bremsstrahlung value, it enhances the coupling efficiency of the laser beam into the workpiece. Secondly, when the ion/electron density is above the Bremsstrahlung value, it

shields off the laser beam from incident onto the workpiece and sometimes defocuses the laser beam [133]. In order to control the density of the ionized species in the plasma cloud to be below Bremsstrahlung value, many plasma control techniques have been developed such as welding in vacuum or reduced atmosphere [134, 135], using high repetition rate pulsed laser [136, 137], shorter wavelength [138] which interfere the growth of the plasma. The most popular technique to reduce the shielding effect of the plasma is the use of a gas side jet such as helium side jet for suppressing the plasma above the keyhole [139].

Tse et al [27, 28] have reported using electric and magnetic field as a plasma control tool during CO₂ laser welding. They have used a group of permanent magnets and a DC power supply to apply magnetic and electric fields. Their results indicated that both fields can influence the shielding effect of the plasma above the keyhole.

It was found that at suitable field parameters the penetration depth can be increased by more than 13%. The experimental results showed that at weak magnetic field strength, the penetration depth increases with decreasing the weld bead width. They have also showed that too strong magnetic field strength can reduce the effectiveness for plasma control. This is due to higher ion/electron density (above a critical value) which reduces the coupling efficiency of the laser beam and consequently reduces the penetration depth.

Tse et al [27] have also reported that using magnetic field alone can influence the shielding effect of the plasma. They have found that at a suitable magnetic field strength the penetration depth increased by about 7%, but no significant difference on the width of weld bead was found. They have found that the effectiveness of using magnetic field for plasma control is directly proportional to the size of the plasma.

A typical problem in laser beam welding with filler is an insufficiently diluted melt pool leading to a non-uniform element distribution in the seam. Gatzen et al [29, 140] have reported effect of electromagnetic stirring on the

element distribution in laser beam welding of aluminum with silicon containing filler wire. They have used additional external electromagnetic field to alter the flow condition inside the melt pool due to induced volume forces and hence to modify the element distribution.

The numerical results showed both the frequency and flux density of the magnetic field have an effect on the filler wire material distribution and the concentration of alloying elements in the weld seam.

Schneider et al [30] have reported that using an electromagnetic field during laser beam welding of aluminum alloys may favor pore outgassing through the top oxide layer. The results showed an oscillating magnetic field reduces the weld pores up to 80% . A similar tendency has been showed for the weld surface roughness which is reduced by around 50%.

In summary, we have reviewed the existing micro/nano laser surface structuring techniques. It showed laser surface structuring based on ablation has been widely investigated , but hardly any report can be found on non-ablative laser surface structuring. Thus, we decided to investigate and develop new technique of non-ablative laser surface structuring.

Literature review also showed the importance of laser produced plasma (LPP) in laser surface structuring, micro/nano machining and the usage of a magnetic field as a control tool of LPP. Controlling LPP using a magnetic field is of great interest since a magnetic field can effectively control the dynamic properties of this transient and energetic plasma. Besides its basic research importance, the effect of a magnetic field on the expansion dynamics of LPP has also gained importance in applied research such as pulsed laser deposition (PLD) techniques, magnetic field assisted laser welding and hardening. However, no report has been found on magnetic field assisted laser surface structuring. Thus, we decided to investigate and develop new technique for magnetic field assisted laser (ns/fs) surface structuring and machining.

Chapter 3: Materials and Experimental Procedures

3.1. Introduction

This chapter will describe the materials used in the study and the experimental procedures. Type of lasers which have been used in the experiments will be explained. Finally, the surface characterization techniques that are used to characterize the irradiated surfaces will be explained.

3.2. Materials

The material mostly used in the study was a single crystal n-type (phosphorous doped) silicon wafer with (100) crystal orientation, resistivity $\rho = 1\text{-}20\ \Omega\cdot\text{cm}$ and thickness of $300\ \mu\text{m}$. The wafers were cut into smaller pieces mostly in the size of 10mm by 10 mm.

In order to wash all contaminations and native oxide out, ultrasonic cleaning of the samples was carried out in methanol for 10 min, acetone for another 10 min, and then de-ionized water for 30 min. To minimize influence of native oxide layer, the cleaned samples were kept in the de-ionized water till being used.

The second material used in the study was Titanium alloy type Ti4Al6V. The Ti4Al6V rectangular bar was cut into pieces in the size of 20mm by 20 mm and the samples were carefully polished using polishing machine with the sandpapers No. 180, 400, 800, and 1200.

Oxygen and argon gas were used as reactant atmosphere in the surface irradiation experiments and were delivered onto the silicon surface in various pressures (0.25, 0.5, and 0.75 bar) through a coaxial nozzle.

3.3. Lasers

3.3.1. Fiber Laser

Fiber laser (SPI 200 W) system in Continuous wave mode with wavelength $\lambda = 1090\ \text{nm}$ was used to irradiate the samples which are mounted on a motorized X-Y precision stage. The output laser beam profile was Gaussian

shape. The laser beam was introduced to the sample surfaces with a lens with focal length of 100 mm. It has excellent beam quality defined by fiber – M^2 - 1.05 with TEM00 spatial mode.

3.3.2. Nanosecond Ultraviolet Laser

The coherent Avia X10W Q-switched diode-pumped solid state (DPSS) ultraviolet (UV) laser system was used in the experiment. The laser wavelength was 355 nm, the laser pulse frequency ranged from 10 kHz to 100 kHz and the pulse duration of the laser beam was 20-35 ns depending on the laser pulse frequency used. The output beam profile was Gaussian shape. The spatial mode was TEM00 ($M^2 < 1.3$). The beam divergence was less than 0.3 mrad. The laser beam with a diameter of 3.5 mm (@ $1/e^2$) was introduced to the sample surface using galvanometer scanner with an f-theta flat field lens of 100 mm focal length. The galvanometer scanner was used to control the laser beam via the PC. Scanning speed could be set at up to 2000 mm/s.

3.3.3. Ti-sapphire Femtosecond Laser

Ti-sapphire femtosecond laser system (Clark-MXR, CPA 2001) which provides high-intensity fs laser pulses using chirped pulse amplification technique was used in the experiment. The pulse duration of the output beam from the amplifier is 150 fs with wavelength of 775 nm. The maximum repetition rate is 1 kHz and the pulse profile is approximately Gaussian shape. The laser was focused on the sample by a plano-convex lens with focal length of 100 mm.

3.4. Surface Characterization Techniques

3.4.1. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained.

Compositional analysis of laser induced textures was conducted by an X-ray diffractometry (Philips PW1710 series). A continuous scan of Cu K α 1 radiation with wavelength of 1.54056 nm was used to acquire compositional patterns of the surface with a step size of 0.02 degree.

3.4.2. Scanning Electron Microscope (SEM)

Scanning electron microscope and field emission scanning electron microscope (JEOL S560 SEM) were used to observe and characterize micro/nano morphology of the laser textured surfaces.

The technique is based on the electron beam-matter interaction. The electron beam interacts with electrons in the sample, producing various signals carrying the information on the sample's morphology and composition.

3.4.3. Energy Dispersive X-Ray Spectroscopy (EDX)

Energy dispersive X-Ray spectroscopy (EDX or also called EDS) has been proved to be a very useful tool for compositional analysis of a surface. It is being used as a popular attachment with most electron microscopes (SEM, TEM, and STEM). It has been used to characterize chemical composition of the irradiated samples.

3.4.4. Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system resulting in the energy of laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar but complementary information.

Renishaw inVia Raman Microscope with 488 and 514nm wavelength with a wide range of excitation power and Raman shift from 100 cm⁻¹ to 3200 cm⁻¹ was used to characterize laser textured surfaces. These results provide us more details about chemical composition of the textured surfaces.

3.4.5. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) has been used widely in materials science and chemistry. It provides atomic composition of sample in a non-destructive manner, as well as other chemical information such as binding constants and oxidation states. Sample under study is subjected to irradiation by a high energy X-ray source. X-rays penetrate only 5-20 Å into the sample allowing for surface characterization rather than bulk chemical analysis.

When an atom absorbs X-ray, its energy will cause electron ejection. The ejected electron has a kinetic energy (KE) that is related to the energy of the incident beam ($h\nu$), the electron binding energy (BE) and the work function of the spectrometer (ϕ) as seen in the following equation.

$$BE = h\nu - KE - \phi_s \quad (3.1)$$

Thus, the binding energy of the electron can be calculated which is resulting into the surface chemical analysis. It has been used to determine more details on the chemical composition and the binding energy of the surface layer of laser formed textures.

3.5. Surface Morphology Techniques

3.5.1. Atomic Force Microscopy (AFM)

Atomic force microscopy is used widely to analyze and characterize the surface structures, morphology and forces of materials at the nanoscale level. It is a very high-resolution type of scanning probe microscopy with the resolution in order of fractions of a nanometer. We have used AFM in the study to determine micro/nano features of the laser-induced textures.

3.5.2. Confocal Microscopy

Confocal microscopy is an optical-based technique used to enhance optical resolution and contrast. It enables to construct the three dimensional structures from the obtained images. This technique has obtained broad usage in life science, semiconductor inspection, and materials science.

Confocal microscopy (NIKON – Eclipse L150) was used in the study to morphologically characterize the laser-textured surfaces. Spatial sampling depends on objectives used. We have used objectives 20 XEPL, 50XEPL and 100XEPL with 0.91 μm , 0.36 μm , and 0.18 μm spatial sampling, respectively.

Chapter 4: Results and Discussion

4.1. Introduction

This chapter will represent and discuss the results obtained during the study. We will divide the chapter to three main sections, (i) infrared fiber laser ($\lambda = 1090 \text{ nm}$) micromachining of silicon, (ii) non-ablative laser surface texturing and (iii) magnetically laser micromachining.

Laser micromachining of silicon using infrared fiber laser will be described and analyzed. The analysis showed that infrared fiber laser is not regarded as a suitable tool for laser micromachining of silicon. Thus, efforts have been made to use the fiber laser in the texturing field rather than micromachining one. The results of laser surface texturing will be shown and described in the section (ii).

Non-ablative laser surface texturing will be described and divided in two sub-sections, thermal and non-thermal non-ablative laser surface texturing. Thermal non-ablative laser texturing has been conducted through CW fiber laser ($\lambda = 1090 \text{ nm}$) and non-thermal non-ablative laser texturing has been also conducted using Ti-sapphire femtosecond laser ($\lambda = 775 \text{ nm}$ and $\tau_p = 150 \text{ fs}$).

Finally, magnetically laser micromachining will be presented and discussed experimentally and theoretically through magnetohydrodynamic (MHD). The results show the successful influence of the external magnetic field on the laser-induced plasma resulting in increased ablation rate.

4.2. Laser Micromachining of Silicon Using Fiber Laser ($\lambda = 1090 \text{ nm}$)

The advantages of fiber lasers (flexible optical delivery, high output power, high optical quality and etc.) make it as an excellent tool in micro/nano laser material processing. Thus, fiber laser as the processing tool and silicon as the material were selected for preliminary study. Table 4.1 shows the laser parameters used to irradiate silicon surface.

Table 4.1 laser processing parameters for ablation of Si

Laser	Fiber laser ($\lambda = 1090 \text{ nm}$)			
Parameters	Repetition rate (kHz)	Laser mode	Feed rate (mm/min)	Laser power (W)
Range	1 - 12	CW/FM/AM	200 - 500	20 - 80

Figure 4.1 (a) demonstrates morphology of the surface irradiated with various laser powers in CW mode. The results showed no ablation and materials removal at the laser power from 20 W to 40 W, as shown in Figure 4.1 (a). When the power increases to 50 W, the depth of kerf also increased to 0.7, 1.1, 1.2, 1.4 μm in various feed rate, 500, 400, 300, and 200 mm/min, respectively. The laser power further increased to 60, 70, and 80 W, but the results showed the low rate of increasing in the depth. The details can be seen in Figure 4.1 (a).

Furthermore, frequency modulated (FM) and amplitude modulated (AM) mode of fiber laser ($f = 12 \text{ kHz}$) were used to irradiate the surface. Figure 4.1 (b) shows that the formation of kerf initiates at the power of 20 W rather than at the laser power of 40 W in CW mode one. It shows that the depth of ablation increased in FM/AM mode of irradiation. The depth details can be seen in Figure 4.1 (b) at the various laser powers and feed rates. However, the formed depth still shows the low material removal.

Figure 4.1 Effect of laser power and scanning speed on the depth of grooves at various (a) CW mode (b) FM/AM modes

Close look at the irradiated area was conducted using surface profiler and scanning electron microscope (SEM). Figure 4.2 shows the typical result of the experiments.

Figure 4.2 Morphology of the irradiated Si surface using fiber laser of 400 mm/min velocity and 40W laser power (a) SEM, (b) Talyscan surface profiler

It is very interesting to observe that the volumetric area is formed few microns above the original surface at the both sides of the kerf, as shown in Figure 4.2. This indicates accumulation of the melt and its solidification before evaporation. This also shows inefficient removal of silicon by fiber laser. We attributed the raised volumes to the melt expulsion and the oxidation of silicon. It is well known that the volume of SiO_2 is 2.16 times of the volume of silicon.

X-ray diffraction (XRD) analysis of the volumes showed presence of silicon oxide, as shown in Figure 4.3. It provides the evidence for the formation of silicon oxide at the edges that is responsible to the volume expansion.

In seeking for the reason of inefficient material removal of silicon by fiber laser, we first explain the absorption of laser light by silicon that is of great importance in laser machining. Furthermore, we explain the hydrodynamic melt expulsion that is mainly responsible for forcing out the molten material in this case. Expelled melt solidifies and oxidizes along the edges causing the swelled volume that can be used somehow to texture the surface. It will be explained in details in the following sections.

Figure 4.3 Typical XRD pattern shows SiO₂ in the laser irradiated sample which indicate oxidation reaction take place during laser process

4.2.1. Absorption of Laser Light

Laser light for causing any obvious effect must first be absorbed. Absorption of laser light by the material is a very important factor in laser processing. It strongly depends on the optical properties of irradiated material [39].

A real laser beam can be approximated by a monochromatic and linearly polarized plane electromagnetic wave. The electric field of propagating wave in a homogenous and non-absorbing medium can be expressed as:

$$E = E_0 e^{i(2\pi z/\lambda - \omega t)} \quad (4.1)$$

where z is the coordinate along the beam propagation direction, ω is the angular frequency, and λ is the wavelength of the beam. The last two parameters are connected to each other through the phase velocity c/n_1 using the following equation; which c is light speed and n_1 is the refractive index of material.

$$\lambda = \frac{2\pi}{\omega} \cdot \frac{c}{n_1} \quad (4.2)$$

Also the same equation as (4.1) exists for the magnetic field of light (H). The magnetic and electric field amplitudes are linked through Equation (4.3) [39]:

$$H_0 = n_1 \epsilon_0 c E_0 \quad (4.3)$$

where ϵ_0 is the dielectric constant in vacuum. The amount of energy carried by the electric and magnetic fields of light is averagely the same. However, the contribution of the magnetic field to the force applied on an electron is smaller than the electric field.

The energy flux per unit area deposited on the material by the electromagnetic field (light) is called irradiance and given by [39]:

$$I = |E \times H| = n_1 \epsilon_0 c E^2 \quad (4.4)$$

Assuming that the irradiance is the maximum near the optical axis and reduces laterally, the distribution of laser beam intensity in cylindrical system can be expressed by Equation (4.5). It is valid for the Gaussian distribution and fundamental mode (TEM₀₀) of resonator.

$$I(r) = I_0 e^{-r^2/w^2} \quad (4.5)$$

where I_0 is the irradiance of laser beam on the axis ($r=0$), and w is the beam radius. The total power of the beam is then [39].

$$P = \pi w^2 I_0 \quad (4.6)$$

In most thermal-based laser processing where the Rayleigh length ($z_R = \pi w^2 / \lambda$) is longer than the optical penetration depth, the Thermal energy deposited by laser beam can be written as [141]:

$$Q(x_\alpha, t) = I(x, y, t)(1 - R)f(z) = I_a g(x, y)f(z)q(t) \quad (4.7)$$

where $I_a = I_0(1 - R)$ is the absorbed or non-reflected laser-light intensity on the surface $z=0$. $g(x, y)$ is the intensity distribution function (beam shape) on the xy-plane. $f(z)$ shows the attenuation of the laser light in z-direction, $q(t)$ is the temporal dependence (pulse shape).

The maximum value for $g(x, y)$ and $q(t)$ is one. $R \equiv R(T, \lambda)$ describes the reflection of laser beam from the irradiated surface that depends on the temperature and incident wavelength.

$f(z)$ is the attenuation function of the laser beam in z-direction which for the uniform material is expressed as the following:

$$f(z) = \alpha(T(z)) \exp \left[- \int_0^z \alpha(T(z')) dz' \right] \quad (4.8)$$

$\alpha(T(z))$ represents the temperature dependent linear absorption coefficient at a certain laser wavelength. In case of α infinite and independent of temperature, the attenuation function can be rewritten as [141]:

$$f(z) = \alpha \exp(-\alpha z) \quad (4.9)$$

In absorbing media the complex refractive index ($n + ik$) is being used rather than real refractive index (n). k is the extinction coefficient defining

how strongly a material can absorb a light at a certain wavelength per mass unit. The absorption coefficient is defined at a particular intensity in the following equation.

$$\alpha = -\frac{1}{I} \frac{dI}{dz} = \frac{2\omega k}{c} = \frac{4\pi k}{\lambda}. \quad (4.10)$$

The parameter $1/\alpha$ is the inverse of the absorption coefficient which represents how far a light can penetrate into a material before completely being absorbed. $1/\alpha$ is known as optical penetration depth or absorption length. As seen in (4.10), the shorter wavelengths can produce high absorption coefficient and then low optical absorption length.

Complex refractive indexes of silicon in the region of fiber laser ($\lambda = 1080 \pm 10\text{nm}$) used in the experiments and their absorption coefficients are listed in Table 4.2.

Table 4.2 Complex refractive index of silicon in the fiber laser region [142]

Wavelength (nm)	$n + i\kappa$	Absorption coefficient (cm^{-1})	Absorption length (μm)
1070	3.5594+i0.0000947368	11.1261	898.8
1080	3.5548+i0.0000421052	4.89	2045
1090	3.5501+i0	≈ 0	$\approx$ infinite

It can be deduced from Table 4.2 that the fiber laser can go through the silicon before completely being absorbed. This explains that silicon is highly transparent to the infrared wavelength of fiber laser ($\lambda = 1090 \text{ nm}$). Thus fiber laser is not regarded as a suitable tool for ablation and micromachining of silicon.

4.2.2. Melt Expulsion Mechanism

Based on driving force on the melt, expulsion of the melt in laser ablation can be mainly caused by:

- (1) Pressure from inside of the melt, and
- (2) Pressure from outside of the melt [143].

4.2.3. Explosive Melt Expulsion in the Form of Droplet

This type of melt expulsion is because of creation of the pressure from inside the melt that can occur in the following cases [143]:.

- (1) For compound materials (polymers and some ceramics). Subsurface overheating causes a fast expulsive volume expansion.
- (2) For metallic alloy with multiple ceramic components. Having different boiling points causes different saturated vapor pressures. During laser irradiation, the elements with lowest boiling point (for example Zn or Mg in the case of metallic alloys) begin to vaporize earlier than other elements which are still in the molten state and do not strongly vaporize. Therefore, the generated vapor pressure inside the molten pool causes explosive removal from the surface.
- (3) For single-element targets (such as metals). Even small amount of contaminant gases embedded in a surface layer of a metal induce its volume evaporation at high temperatures. It can dominate usual surface evaporation particularly in high intensities resulting in an explosive sputtering of the melt.

4.2.4. Hydrodynamic Melt Expulsion along the Spot

This melt expulsion is originated due to the pressure gradient of the vapor (plasma) on the molten surface. The pressure of the vapor (plasma) is different at the center and at the periphery of the irradiated spot. This expulsion is mainly responsible for the resolidified material across the border of the spot. Preventing this melt movement toward the border is of great importance to get clean laser ablation. Surface roughness and spatial distribution of the beam

could be also the cause of pressure non-uniformities on the irradiated surface [143].

Based on the absorptivity analysis of Si at the given wavelength ($\lambda = 1090 \text{ nm}$) and obtained results, the lateral expulsion along the surface induced by the plume pressure is considered as the possible mechanism responsible for melt accumulation at the border.

4.2.5. Melt Depth Analysis and Effect of Low Absorption

As it is discussed in section 4.3, there is low absorption of silicon to the infrared wavelength of fiber laser ($\lambda = 1090 \text{ nm}$) and consequently weak evaporation. With the assumptions of top-flat intensity distribution and volumetric heating ($(1/\alpha) \gg 2\sqrt{D_{th}\tau}$) at the end of pulse duration ($t = \tau$) the melt depth (h) can be expressed using the following equation [39]:

$$h(I_a) = (1/\alpha) \ln(I_a/I_{ma}) \quad I_a \geq I_{ma} \quad (4.11)$$

where I_a and I_{ma} are absorbed intensity and threshold intensity for melting at normal incidence, and D_{th} is thermal diffusivity.

The threshold intensity for melting can be expressed as the following:

$$I_{ma} = C\rho(T_m + T_q - T_i)/(\alpha\tau) \quad (4.12)$$

where T_m is the melting temperature, $T_q = q_m/C$ in which q_m is the latent heat of melting, T_i is the initial (ambient) sample temperature, C is the heat capacity, and ρ is the material density.

The melt depth (h) can be rewritten in terms of the temperature reached at the surface at the end of the laser pulse with a particular intensity (I) (i.e. $T = T(I)$) [143]

$$h(T) = (1/\alpha) \ln[(T + T_q - T_i)/(T_m + T_q - T_i)]. \quad (4.13)$$

where T is the surface temperature and T_i is initial temperature of silicon.

As shown in Figure 4.4, the full surface profile of the irradiated spot includes two main parts:

- (1) Moving part in which main laser absorption and material removal takes place, and
- (2) Stationary part in which there is practically no material removal.

Figure 4.4 Melt expulsion and location of stationary and moving area in the laser irradiated area

Due to pressure gradient between the bottom and entrance of the kerf which is induced by evaporation in the bottom, the vapor (plasma) flow create a certain drag force on the melt on the stationary part, as shown in Figure 4.4.

This induces the melt motion toward the border, solidification of the melt and formation of the raised volumes that are mainly composed of silicon oxide.

As a result of these two expulsion effects, melt mobility and melt displacement is high. Thus, the surface temperature on the stationary part can be considered as equal to the melting temperature (T_m). On the other hand, due to the low absorption of the fiber laser on silicon and resulting shallow spot, the temperature of the stationary part and the surface temperature can be taken equal ($T = T_m$). Therefore regarding to Equation (4.13), it is deduced that melting depth in this case is nearly negligible ($h(T) \approx 0$). This was indeed found to be the case.

The results and analysis shows that the fiber laser with the infrared wavelength ($\lambda = 1090$ nm) could not be regarded as a suitable tool for ablative texturing or micromachining of silicon. However, the formed oxide volume at the spot border brings the idea to our mind that it could be used somehow for texturing the surface rather than machining and material removal. Application of the laser for texturing the surface is presented in the following section.

4.3. Non-ablative Texturing of Silicon Surface – Thermal basis

4.3.1. Introduction

Surface texturing is an important research area with a broad range of applications. The laser ablation-based surface texturing has been well studied. Micron and submicron texturing of silicon by laser ablation [1-5] has drawn strong interest due to its wide use in microelectronics and solar cells. Several groups have also reported use of pulsed lasers to produce grooves [6] or pits [7] on surfaces of many other materials such as Ge [8], metals [9] and thin films [10] under diverse experimental conditions. Near-field enhanced laser irradiation with micro-nano sized spheres [11, 12] and near field scanning optical microscope (NSOM) [13, 14] are used to form micron, submicron, and

nano patterns, but the approaches are also based on the target *ablation* and redistribution of melt materials.

Hardly any reports can be found in the public domain on use of non-ablative laser surface texturing to form uniform micro-bumps. Silicon is known to be highly transparent to the infrared wavelength of fiber laser ($\lambda=1090$ nm), so fiber laser is not regarded as a suitable tool for ablative texturing of silicon. However, we recently developed a novel technique to pattern Si surface by *non-ablative* laser texturing using continuous wave fiber laser ($\lambda=1090$ nm) that the results have been published in [15, 16].

4.3.2. Material and Experimental Procedures

The material used in the study was a single crystal n-type (phosphorous doped) silicon wafer with (100) crystal orientation, resistivity $\rho = 1\text{-}20\ \Omega\cdot\text{cm}$ and thickness of 300 μm . The wafer was cut into smaller pieces in the size of 10 mm by 10 mm.

Ultrasonic cleaning of the samples was carried out in methanol for 10 min, acetone for another 10 min, and then de-ionized water for 30 min. To minimize influence of native oxide layer, the cleaned samples were kept in de-ionized water till being used.

The samples were mounted on a motorized X-Y precision stage and irradiated using a CW fibre laser with wavelength $\lambda = 1090$ nm. The laser scanning was carried out in an area of 2 mm by 2 mm with a point scanning pitch of 20 μm , as shown in Figure 4.5. A lens of 50 mm focal length was used to focus the laser beam to the size of $\approx 20\ \mu\text{m}$.

Figure 4.5 Illustration of experimental setup for fiber laser point scanning of Si surface

The laser experiments were carried out at a fixed dwell time of 40 ms but using varying laser power (11.5, 19, 23.3 or 29.3 W) in either ambient, oxygen or argon gas atmosphere. Oxygen and argon were delivered onto the Si surface in three different pressures (0.25, 0.5, or 0.75 bar) through a coaxial nozzle with an exit diameter of 2 mm and placed about 2 mm above the surface, as shown in Figure 4.5. .

The laser irradiated surfaces were characterized using a confocal microscope. Energy dispersive X-ray spectroscopy (EDX) was used to examine chemical composition of the surface features.

4.3.3. Surface Characterization Results and Discussion

Surfaces irradiated with the fiber laser in various conditions were carefully characterized. At the lowest power of 11.5 W, no morphologically modified surfaces were observed. When the power was increased to 19 W, the laser was able to change morphology of the surfaces. The typical results are shown in Figures 4.6 and 4.7.

After the irradiation in the ambient environment, the surfaces were found to be roughened without regular patterns, as shown in Figure 4.6(a). It is very interesting to observe that the irradiated surfaces rose a few microns above the original surface, as shown in Figure 4.7(a). This indicates swelling of the material during the laser irradiation. We attribute the swelling to laser-induced thermal oxidation of Si. It is well known that 56% of the oxide thickness lies above the original surface if a bare silicon surface is oxidized. Indeed, EDX analysis of the laser irradiated surface showed the presence of silicon oxide.

If thermal oxidation is really the cause of the swelling in the ambient environment, then no such swelling should be expected to occur during the laser irradiation in the inert environment of Ar. This was indeed found to be the case. The laser irradiation of Si in Ar resulted in roughened irregular surfaces (Figure 4.6(b)) but the average surface height is at the original surface level, as showed in Figure 4.7(a). EDX analysis of the surface irradiated in Ar did not detect any oxygen, as shown in Figure 4.8(a).

Figure 4.6 Confocal microscope images of the Si surface irradiated using laser power 19 W and dwell time 40 ms (a) in ambient, (b) in Ar (0.5 bar), (c) in O_2 (0.25 bar), (d) in O_2 (0.5 bar) and (e) in O_2 (0.75 bar) [15].

Figure 4.7 Profile of the Si surface irradiated using laser power 19 W and dwell time 40 ms (a) in ambient and Ar, (b) in O_2 (0.25 bar), (c) in O_2 (0.5 bar) and (d) in O_2 (0.75 bar) [15].

It was decided to investigate on use of the laser-induced thermal oxidation to produce regularly-patterned surface bumps. To this aim, Si surfaces were irradiated in pure O_2 to enhance oxidation.

Various laser powers (11.5, 19, 23.3 or 29.3 W) were tried. At the lowest power of 11.5 W, the laser was found to be too weak to modify morphology of the Si surfaces. When the laser power was increased to 19 W, uniformly patterned submicron bumps were formed under either of the three different O_2 pressures (0.25, 0.5, or 0.75 bar), as shown in Figures 4.6(c)-(e) and 4.7(b)-(d). When the laser power was further increased to 23.3 W or 29.3 W, the regular bumps disappeared and the surface patterns became random.

EDX was used to examine chemical composition of the laser-induced submicron bumps. Silicon and oxygen were detected, as shown in Figure 4.8, indicating that the bumps are made of silicon dioxide.

The oxidation of Si can be attributed to heating under irradiation of the laser. It can be deduced that only localized heating can lead to formation of the regular bumps. This explains why uniform patterned surface was achieved only within a narrow processing window (power of 19 W). When laser power was too high, surface melting occurred, resulting in random surface patterns.

Figure 4.8 EDX spectrum of (a) Si surface irradiated in Ar and (b) Si surface irradiated in O_2 [15].

Figure 4.9 shows schematically the conventional growth of SiO_2 using uniform heating source. The uniform heating oxidizes the Si surface uniformly and thus produces uniform swelling of the surface due to formation of SiO_2 , as shown in Figure 4.9(b). In this case, no discrete bumps are formed on the surface.

Figure 4.9 Schematic diagram of SiO₂ growth on Si surface by uniform heating source, showing the changes in thickness (a) before oxidation, and (b) after thermal oxidation [15].

Figure 4.10 shows schematically the irradiation required for ablative and non-ablative laser surface texturing. When the laser power (intensity) is above the ablation threshold as shown in Figure 4.10(a), it will texture the surface on ablative basis. However, when the laser power is lower than the ablation threshold and in the meantime high enough to trigger the oxidation (i.e. located in laser-induced oxidation zone) as shown in Figure 4.10(b), it will texture the surface on non-ablative basis. Finally, if the laser power is lower than the oxidation threshold as shown in Figure 4.10(c), it will not cause any morphological changes on the surface.

Figure 4.10 Illustration of the irradiation for (a) ablative texturing, (b) non-ablative texturing, and (c) no-surface modification.

When the laser beam moves from one point to another (as illustrated in Figure 4.5), it acts as a localized point heating source, therefore formation of discrete bumps is expected to occur at the laser dwelling locations if the laser power is sufficiently high to activate rapid oxidation and in the meantime low enough to avoid surface melting, as shown schematically in Figure 4.11(a). It can be seen from Figure 4.7 that pitch of the bumps is $20\text{ }\mu\text{m}$ and it indeed matches the laser scanning pitch, providing further support to the above analysis.

Introducing O_2 flux into the locally heated region could provide more diffusive and oxidizing atmosphere and therefore help to enhance the laser-induced thermal oxidation process, making it easier to form surface bumps.

Figure 4.11(b) illustrates the microscopic mechanism of the laser-induced thermal oxidation (photothermal oxidation). For photon energies (i.e., $E_{\text{photon}} = h\nu$) near Si bandgap (1.12 eV) the enhancement in oxidation rate is mainly due to the laser surface heating and the increased electron population in the Si-SiO₂ interface. Considering that Si bandgap decreases with increasing temperature [44], laser radiation with the 1090 nm wavelength ($E_{\text{photon}} = 1.138\text{ eV}$) causes the electron emission from Si into the Si-SiO₂ interface and O_2 diffusion. The electrons are also transferred from Si to

adsorbed O_2 and enhance the diffusion of O_2 through the oxide layer, as shown in Figure 4.11(b). Therefore, electron tunneling and O_2 diffusion may explain the initial rapid oxidation.

Figure 4.11 (a) Laser-induced SiO₂ bumps by localized Gaussian heating source; (b) microscopic model for the laser-induced surface oxidation, ↑ and ↓ indicate increasing and decreasing concentrations, respectively [15].

A further enhancement of the oxidation rate by the laser radiation is due to the heating of both the oxide and Si which favors the O_2 diffusion and the hot electrons emission. On the way towards the Si-SiO₂ interface, O_2 will pick up electrons which are trapped in the oxide. As a result, the concentration of O_2 decreases, while that of O_2^- increases. Diffusion of O_2^- is also enhanced by the electric field related to the positively charged holes at the Si surface. In the layer near to Si-SiO₂ interface, diffusion of O_2^- and O_2 becomes blocked due to lattice mismatch. However, hot electrons emitted into the SiO₂ can easily penetrate the blocking layer and enhance the oxidation rate.

The O_2 pressures were found to affect the bump height. At the pressure of 0.25 bar, the height was found to be 850 nm. When the pressure was increased to 0.5 bar, the bump height decreased to 720 nm. Increase of the pressure further to 0.75 bar resulted in bumps with even lower height (660 nm). Though introducing oxygen flux provides more oxidizing atmosphere, it enhances the convective dissipation of thermal energy and thus slows the oxidation rate.

Potential industrial applications of this process are: (i) flexible, selective and fast local rapid thermal oxidation; (ii) debris-free wafer marking and SiO₂ structures for optical uses, and (iii) surface textures for new surface functionality.

We explained the non-ablative surface texturing in terms of laser-induced localized thermal oxidation [15, 16]. However, the proposed mechanism is based on qualitative analyses only. Finite element method is chosen to gain better understanding of the non-ablative texturing mechanism. Since it has been used successfully to study laser processing of materials [17-22] and in particular thermal oxidation of Si [23-25].

As the laser experiments were carried out using varying laser power (11.5, 19, or 23.3 W) and dwell time (10, 20, 30, or 40 ms) in O₂ atmosphere, surface irradiated with the fiber laser were again carefully observed under scanning electron microscope (SEM). We summarize our observation as follows and will attempt to explain the phenomena by numerical method.

- (1) No discernible change was found on surface irradiated using the lowest power of 11.5 W.
- (2) Considerable morphological changes were found on surface irradiated with the highest power of 23.3 W, but the surface patterns were irregular, as shown in Figure 4.12(a).
- (3) When the moderate power of 19 W was used, regularly patterned surface features were formed when the dwell time was 40 ms, as shown in Figure 4.12(b); however, no such uniform surface patterns were observed for the lower dwell times (10, 20, or 30 ms). The regularly patterned surface was further studied using atomic force microscope (AFM), as shown in Figure 4.13(a). Figure 4.13(b) shows the profile of the bump.

Figure 4.12 SEM images of surface irradiated with (a) laser power of 23.3 W, dwell time of 40 ms and (b) laser power of 19 W, dwell time of 40 ms.

Figure 4.13 (a) AFM image of surface irradiated with laser power of 19 W and dwell time of 40 ms. (b) 2D profile of a bump shown in (a).

4.3.4. Numerical Simulation - Finite Element Model of 2D heat equation

The diffusion of heat is governed by the heat equation, which follows from the Fourier law and conservation of energy. The Fourier law

$$\vec{\phi} = -k\nabla T \quad (4.14)$$

states that local heat flux $\vec{\phi}$ is proportional to the temperature gradient ∇T . Note that thermal conductivity k generally varies with temperature and direction in anisotropic materials, in which case k becomes a tensor. In the following we consider these dependencies.

Assuming no work is being performed, the change in internal energy per unit volume ΔQ is proportional to the change in temperature ΔT ; that is,

$$\Delta Q = c_{es} \rho \Delta T. \quad (4.15)$$

We now assume that the equivalent heat capacity c_{es} and the mass density ρ are both temperature dependent. The heat equation is a second-order partial differential equation (PDE), specifically it is a parabolic PDE. We used FE commercial code (COMSOL Multiphysics) to solve the time dependent heat equation. More detail on FE theory can be found in [144].

Two-dimensional (2D) finite-element model was used to study the temperature rises caused by laser irradiation at different laser powers and dwell times. The XY coordinate system adopted is shown schematically in Figure 4.14. The incident beam was perpendicular to the sample surface with the size of $1 \text{ mm} \times 1 \text{ mm}$.

Figure 4.14 Illustration of Si surface irradiation model for thermal analysis. O, center point of the Si surface; X and Y, the 2D coordinate axis [145].

The transient temperature field can be calculated by solving the following heat-conduction equation [17, 146, 147],

$$\rho(T)c_{es}(T)\frac{\partial T(x,y,t)}{\partial t} = \nabla[k(T)\nabla T(x,y,t)] + q \quad (4.16)$$

where $T(x,y,t)$ represents the temperature distribution at time t and position (x,y) , and $\rho(T)$ and $k(T)$ are temperature-dependent density and thermal conductivity of Si. The equivalent heat capacity is defined as [17, 146, 147],

$$c_{es}(T) = c_s(T) + H_{sl}\delta(T - T_{melt}) \quad (4.17)$$

where $c_s(T)$ and H_{sl} are the temperature-dependent specific heat and the latent heat of substrate for melting. In addition, $\delta(T - T_{melt})$ is the singular Dirac-delta function in order to treat of latent heat of fusion.

By assuming the incident laser beam to be of Gaussian spatial distribution (TEM_{00}), heating source (q) can be described as [146, 147],

$$q = I_0(1 - R)\alpha \exp\left(\frac{-2(x^2 + y^2)}{w^2}\right) \quad (4.18)$$

where I_0 is the incident laser peak power density at the spot center. R and α represent the reflectivity and absorption coefficient of the Si surface, respectively. w is beam radius at the $1/e^2$ of the peak intensity.

Laser power meter generally measures average power then using duty cycle (the fractional amount of time the laser is "on" during any given period $\equiv t_{pulse}/T = P_{ave}/P_{peak}$), one can easily calculate the peak power. In the study, we used CW laser so average and peak power have the same value. I_0 , the incident peak power density at the spot center, is calculated using $I_0 = P_{average\ power} / (\pi w^2)$.

The boundary conditions are,

$$\left(-k \frac{\partial T(x, y, t)}{\partial x}\right)_{x=\pm a/2} = \left(-k \frac{\partial T(x, y, t)}{\partial y}\right)_{y=\pm b/2} = 0 \quad (4.19)$$

It describes the boundary condition in which the heat flux is zero (Neumann condition). This is due to very small size of laser spot diameter (20 μm) comparing with the model size (1 mm $\times$ 1 mm) and also low thermal conductivity of silicon.

The initial condition is,

$$(T(x, y, t))_{t=0} = T_0 \quad (4.20)$$

where T_0 is the room temperature, which is taken as 300 K.

4.3.5. Numerical Simulation - Material Parameters

The initial temperature is 300 K, the laser spot diameter is 20 μm , and the model size is 1 mm $\times$ 1 mm. The thermophysical and optical properties including the density, specific heat, thermal conductivity, absorption coefficient, and reflectivity are listed in Table 4.3. Most of the parameters vary with the temperature. During the solid-liquid phase transition process, the temperature remains unchanged at the melting point ($T_{\text{melt}} = 1690 \text{ K}$). The melting latent heat of Si is $1.802 \times 10^6 \text{ J/kg}$. The phase change latent heat (H_{sl}) is considered to be the enthalpy of material, written as,

$$H_{sl} = \int \rho c(T) dT \quad (4.21)$$

Table 4.3 Thermophysical and optical properties of Si [142]

The thermophysical parameters	Solid state					Liquid state
$\rho (\text{kg} / \text{m}^3)$	2330					2530
T (K)	300	500	1000	1500	1689	1690
$c(T) (\text{J} / (\text{kg} \cdot \text{K}))$	700	790	970	1080	1100	1100
$k(T) (\text{W} / (\text{m} \cdot \text{K}))$	120	63	27	20	17	63
The optical parameters	Solid state					Liquid state
$\alpha (\text{cm}^{-1})$	50					8.6×10^5
R	0.33					0.72

4.3.6. Modeling in COMSOL Multiphysics

The commercial software, COMSOL Multiphysics, was employed to solve the governing equations using the finite element method. The free triangular

element was used, and for numerical stability and sufficiently high temporal and spatial resolutions, the element size was chosen to be less than one fifth of the laser beam wavelength, and numerical time step was on the order of 10 μ s. The typically simulated time period in this study is up to 40 ms.

Some important settings for the present COMSOL model are listed below:

- (1) Treatment of the latent heat of fusion: the singular Dirac-delta function, $\delta(T - T_{melt})$ is replaced by Gaussian-pulse function defined in “*Scalar Expression*” as

$$f_{guass} = \frac{\exp(-(T - T_{melt})^2 / (\delta T)^2)}{\sqrt{\pi} \times \delta T} \quad (4.22)$$

where δT , melting temperature span of Si, was chosen to be 1 K.

- (2) Temperature-dependent thermal properties: temperature-dependent thermal properties including thermal conductivity and specific heat as listed in Table 4.3, were stored in “*Interpolation Functions*” as a text file.

4.3.7. Simulation Results and Discussion

Simulation results of the temperature evolution at the center of the irradiated point are shown in Figure 4.15. The figure shows that the surface temperature is above the melting point (1690 K) for the highest power of 23.3 W. This explains why no regular surface patterns (Figure 4.12(a)) formed on the surface irradiated with the highest laser power.

It can be seen from Figure 4.15 that no melting occurs on surfaces irradiated with the lower laser powers of 11.5 W and 19 W for various dwell times used. If localized thermal oxidation of Si accounts for formation of the regular bumps as suggested earlier [15], regular bumps might be expected to form for laser power of both 11.5 W and 19 W. However, in reality, regular

surface bumps were formed only when the laser power was 19 W and the dwell time was 40 ms. The quantitative results obtained can help to explain why this is the case.

Figure 4.15 Temperature evolution graph at the spot center irradiated with various laser powers (11.5, 19, and 23.3 W) at the dwell time of 10, 20, 30, and 40 ms [145]

It is found in many studies [148-152] that thermal oxidation of Si surface generally occurs in the temperature range 1000–1600 K and that 56% of the oxide thickness rises above the original silicon surface. For the laser power of 11.5 W used, the peak temperature is around 600 K (Figure 4.15), which is well below 1000 K; therefore, it is understandable why no surface bumps were formed due to thermal oxidation for this laser power.

For laser power of 19 W, the peak temperature is above 1000 K for all the four dwell times used (10, 20, 30, and 40 ms). However, it is noted that regular bumps formed only when the longest dwell time was used. This interesting

phenomenon is believed to be related to decrease of activation energy of Si oxidation with increasing temperature.

Activation energy of Si oxidation lies around 2-2.5 eV for temperature range 1100 to 1200 K, but the value decreases to 1.3 eV when the temperature reaches 1250 K [150]. In the current study, an infrared laser with wavelength 1090 nm was used. Photon energy for this laser is calculated as $E_{\text{photon}} = 1.138$ eV. When the temperature is below 1250 K, the photon energy is well below the activation energy of Si oxidation (which is 2-2.5 eV for temperature range 1100-1200 K and 1.3-2 eV for temperature range 1200-1250 K [150]), making it difficult for effective Si oxidation to occur at temperatures below 1250 K. When the laser power is 19 W and dwell time is 10 ms or 20 ms, the peak temperature is below 1250 K (Figure 4.15), so no effective Si oxidation occurs.

When the temperature rises to 1250 K, the activation energy of Si oxidation is reduced to 1.3 eV, which is very close to but still above the value of photon energy (1.138 eV). When the temperature rises further, the activation energy reduces further. Therefore, at a certain temperature above 1250 K, the activation energy falls below the photon energy, making it possible for the effective oxidation of Si to occur and resulting in localized surface expansion and bump formation.

For laser power of 19 W and dwell time of 30 ms, the peak temperature is just above 1250 K (Figure 4.15). The fact that no bumps were observed on the laser irradiated surface suggests that the activation energy at this peak temperature is not yet reduced to below the photon energy level.

When the dwell time is increased to 40 ms, the peak temperature increases to around 1300 K (Figure 4.15). The fact that bumps were observed on the laser irradiated surface indicates that the activation energy at 1300 K is reduced to below the photon energy. It can be deduced from the analyses that the critical temperature for effective oxidation of Si is somewhere between 1250 and 1300 K. The temperature of 1250 K is used as the lower boundary for effective oxidation, and the upper boundary is naturally the melting point (1690 K).

Figure 4.16 shows the spatial profile of the Si surface temperature at various laser powers at fixed dwell time of 40 ms. For the laser power of 11.5 W, the temperature of the whole irradiated spot remains well below the effective oxidation region. The irradiation at the moderate laser power of 19 W increases the spot temperature so that its central region crosses the effective oxidation temperature. It is also shown in Figure 4.16 that the laser power of 23.3 W brought the irradiated spot into the melting zone and it is the reason to get roughened surface (as shown in Figure 4.12(a)).

Figure 4.16 Temperature profile of the laser spot at various laser powers and dwell time of 40 ms [145].

Furthermore, the numerical simulation can be used as a tool to predict a wide range of laser parameters suitable for making oxide bumps through the non-ablative method. As shown in Figure 4.17, various combinations of laser power and dwell time which fall between the two temperature boundaries lines can be used for the purpose of surface texturing.

Figure 4.17 Map of laser power vs dwell time obtained through simulation, showing the effective oxidation zone to produce regular bumps on Si surface [145].

4.3.8. Surface Properties - Surface Reflection

Optical property of the textured surface was examined through reflection measurement. White light was used to illuminate the surface. Focusing lens at the end of the fiber was used to focus the light. Reflected light from the surface was detected by HR4000 High-Resolution spectrometer and analyzed using SpectraSuite software. Focusing lens on the holder was adjusted to expose the surface perpendicularly, as shown in Figure 4.18.

Figure 4.18 Setup for the measurement of surface reflectivity.

The results show 20-50% reduction in the surface reflectivity, as shown in Figure 4.19. It implies that the technique has the potential to fabricate anti-reflection surfaces.

Figure 4.19 Reflection spectra of textured area in different conditions

There are two kind of light reflection occurring on the surface:

- (1) Specular reflection, and
- (2) Diffuse reflection (scattered reflection).

Based on surface roughness and surface color, one of them can be dominant. However, in most textured surfaces there is combined mode of these reflections. The measurement is the combination of these two reflections.

Reduction in overall reflection coefficient is not only due to the surface textures but also due to the surface composition. Based on the characterization results, it is deduced that decrease in reflection coefficient might be also due to formed silicon oxide that has low reflection coefficient compared to that of silicon.

4.3.9. Surface Properties - Surface Contact Angle (CA)

Surface energy of the Si surface irradiated using laser power 19 W was measured through the measurement of contact angle, as shown in Figure 4.20. Contact angle of as-received Si surface was measured to be 57° , as shown in Figure 4.20(a). However, contact angle of the Si surface irradiated in O_2 (0.5 bar) was increased to 72° , as shown in Figure 4.20(b) due to the formation of uniform array of submicron bumps. The measurement was also conducted for the surface irradiated in ambient. Contact angle was found to be 33° , as shown in Figure 4.20(c) indicating decrease in the surface energy and increase in the surface wettability.

Figure 4.20 Contact angle of the Si surface irradiated using laser power 19 W (a) as-received, (b) in O_2 (0.5 bar), and (c) in ambient.

Furthermore, contact angle of the Si surface irradiated in various pressures of O_2 was measured, as shown in Figure 4.21. It can be observed that contact angle shows decreasing trend as O_2 pressure increases, as shown in Figure 4.21(a)-(c).

Figure 4.21 Contact angle of the Si surface irradiated using laser power 19 W (a) in O₂ (0.25 bar), (b) in O₂ (0.5 bar), and (c) in O₂ (0.75 bar).

4.4. Non-ablative Texturing of Silicon Surface – Non-Thermal basis

4.4.1. Introduction

As it is said in section 4.5.1, surface texturing has become as an important area in scientific research. The laser ablation-based surface texturing has been well investigated for micron and submicron texturing of silicon. However, the approaches are based on the target ablation and redistribution of melt materials.

Non-ablative laser surface texturing which could be based on thermal or non-thermal mechanism has not been well studied. Few works have been just reported on non-ablative laser texturing of silicon surface which are thermal basis, using continuous wave fiber laser [15] or high repetition rate (MHz) femtosecond laser pulses [153] to accumulate thermal effect for thermally induced non-ablative texturing. However, we used low repetition rate (1 kHz)

of femtosecond laser pulses with negligible thermal accumulation and succeeded in non-ablative direct writing of silicon surface. The approach is shown to be based on laser-induced localized non-thermal oxidation of silicon that will be explained in the following sections.

4.4.2. Material and Experimental Procedures

The material used in the study was a single crystal n-type (phosphorous doped) silicon wafer with (100) crystal orientation, resistivity $\rho = 1\text{-}20\ \Omega\cdot\text{cm}$ and thickness of $300\ \mu\text{m}$. The wafer was cut into smaller pieces in the size of $10\ \text{mm} \times 10\ \text{mm}$.

Ultrasonic cleaning of the samples was carried out in de-ionized water for 20 min and then in ethanol for another 10 min. The samples were mounted on precision stage and irradiated using with a femtosecond laser with wavelength $\lambda = 775\ \text{nm}$, pulse duration $\tau_l = 150\ \text{fs}$, and pulse repetition rate $f = 1\ \text{kHz}$, as shown in Figure 4.22. IDI LASER scanning system was used to scan the surface. The laser experiments were carried out in ambient at a fixed scanning speed of $1\ \text{mm/s}$ with laser powers ranging from $5\ \text{mW}$ to $100\ \text{mW}$. A lens of $100\ \text{mm}$ focal length was used to focus the laser beam to the size of $\approx 15\ \mu\text{m}$.

The laser irradiated surfaces were observed using a confocal microscope. Energy dispersive X-ray (EDX) and Raman spectroscopy were used to analyze chemical composition of the swelled lines.

Figure 4.22 Illustration of experimental setup for femtosecond laser scanning of Si surface

4.4.3. Surface Characterization Results and Discussion

Surfaces irradiated with the femtosecond laser in various powers (100, 50, 20, 10, 6, 5 mW) were carefully characterized. At the lowest power of 5 mW, no morphologically modified surfaces were observed. When the power was increased to 6 mW, the laser was able to change the morphology of the surfaces. Typical results are shown in Figure 4.23 and Figure 4.24.

After the irradiation at the highest power of 100 mW, the surface was found to be highly ablated in the groove of about 3.1 μm depth, as shown in Figure 4.23(a) and Figure 4.24(a). When the power was decreased to 50, 20 and 10 mW, the surfaces were also found to be ablated in the groove of about 1.8, 1.1, 0.8 μm depth respectively, as shown in Figures 4.23(b), 4.23(c), 4.23(d), 4.23(b), 4.23(c) and 4.23(d).

When the power was further decreased to 6 mW, a swelled line was observed on the irradiated surface, as shown in Figure 4.23(e) and Figure 4.24(e). Finally at the lowest power of 5 mW, no measurable changes in morphology were observed, as shown in Figure 4.23(f) and Figure 4.24(f).

With carefully controlling laser power, it is very interesting to observe that the irradiated surfaces rose above the original surface as swelled line with about 1 μm height and 10 μm width at the base, as shown in Figure 4.23(e) and Figure 4.24(e). This indicates swelling of the material during the laser irradiation with no ablation. We mainly attribute swelling to laser-induced oxidation of Si. It is well known that 56% of the oxide thickness lies above the original surface if a bare silicon surface is oxidized [154].

Figure 4.23 Confocal microscope images of the Si surface irradiated using various laser powers (a) 100 mW, (b) 50 mW, (c) 20 mW, (d) 10 mW, (e) 6 mW, (f) 5 mW.

EDX was used to examine chemical composition of the laser-induced swelled lines. The results show the high concentration of oxygen in irradiated lines that is believed to be due to Si-O-Si bounds, as shown in Figure 4.25(a). Raman spectroscopy was conducted to confirm the elemental composition of the swelled lines. The experiment was carried out at room temperature using 632 nm of HeNe laser source. The results showed sharp peak at the wavenumber of 519 cm^{-1} that is the characteristic peak of Si. A hump was also

observed at the wavenumber of 954 cm^{-1} indicating that the swelled line is made of silicon dioxide [153], as shown in Figure 4.25(b).

Figure 4.24 Profile of the Si surface irradiated using various laser powers (a) 100 mW, (b) 50 mW, (c) 20 mW, (d) 10 mW, (e) 6 mW, and (f) 5 mW.

Figure 4.25 (a) EDX result of irradiated area, (b) micro-Raman spectroscopy result of irradiated area.

The oxidation of Si can be attributed to heating under the laser irradiation. If thermal oxidation is the only cause of the swelling as shown in [15] and [153], then no such swelling should be expected to occur during the laser irradiation using low repetition rate (1 kHz) femtosecond pulsed laser with negligible heat accumulation. However, the oxidation of Si can also occur through non-thermal mechanisms. Thus, it was decided to investigate the laser-induced non-thermal oxidation method to write on Si surfaces. To this aim, Si surfaces were irradiated in ambient using low repetition rate (1 kHz) femtosecond pulsed laser. Indeed, the non-ablative Si surface writing was achieved only within a narrow processing window (power of 6 mW).

When laser power was higher than the ablation threshold extensive surface melting and ablation occurred, resulting in random surface patterns and grooves. Thus, we kept the power at a level between laser-induced oxidation and ablation threshold.

Generally, the growth of an oxide layer could be described through a fundamental thermal model [152]. Various thermal models have shown that the thermal oxidation of Si occurs at the temperatures in the range of 700 – 1300 °C (1000 – 1600 K) [148, 149, 151, 152]. Thus we used the heat conduction model to estimate the surface temperature.

For simple estimation of the heat accumulation, the complex energy redistribution on the femtosecond time scale is neglected. The analytical solution of the linear heat equation could be used to describe the pulsed-laser irradiation of a semi-infinite substrate with surface absorption and temperature-independent material parameters with a Gaussian beam.

For a single rectangular pulse, the surface temperature rise, ΔT , at the centre of the laser spot ($x=0, y=0$) and for times $t \gg \tau_l$, can be well approximated using the following formula [44].

$$\Delta T(x=0, y=0, t \gg \tau_l) = \frac{I_a w_0^2 \tau_l}{4\sqrt{\pi k t} \sqrt{D t}} \quad (4.23)$$

where I_a is the absorbed laser-light intensity, w_0 is the radius of the laser focal spot, τ_l is the pulse duration, k is the thermal conductivity, D is thermal diffusivity and t is the pulse period. For ultra short irradiation ($\approx$ fs) that the pulse-on time is very short compared to pulse period ($t \gg \tau_l$), Equation (4.23) could be used to calculate the surface temperature rise at the end of the pulse-off time right before beginning of the next pulse. Pulse period is given by $t = 1/f$ in which f is the pulse frequency.

The absorbed laser-light intensity, I_a , can be estimated by the reflection coefficient, R , at the $\lambda = 775$ nm, residual energy coefficient, K , laser power, P , pulse frequency, f , and laser spot radius, w_0 [153].

$$I_a = K(1-R)I_{incident} = K(1-R)\frac{P}{\pi w_0^2 \tau_l f} \quad (4.24)$$

With substituting Equation (4.24) in Equation (4.23), it is simplified to Equation (4.25) which can be used to calculate the surface temperature rise at the end of one pulse.

$$\Delta T = \frac{K(1-R)P}{4k\sqrt{\pi^3 Dt}} \quad (4.25)$$

With the diameter of the focused laser spot, $d = 15$ μm , and laser beam scanning speed, $V_{scan} = 1$ mm/s, approximate number of pulses can be estimated by:

$$N = \frac{d \cdot f}{V_{scan}} \quad (4.26)$$

Eventually, the accumulated temperature rise at the end of N^{th} pulses is T :

$$T = N \cdot \Delta T \quad (4.27)$$

Since the reflection coefficient of silicon during femtosecond irradiation has been shown to be 0.393 for $\lambda = 488$ nm and 0.329 for $\lambda = 800$ nm in [155], we estimated the reflection coefficient to be around 0.33 for $\lambda = 775$ nm. Study done in [156] has shown K to be around 0.8 for fluence less than the ablation

threshold. The thermal conductivity (k) and the thermal diffusivity (D) of silicon are $155 \text{ W/(m}\cdot\text{K)}$ and $8.5 \times 10^{-5} \text{ m}^2/\text{s}$, respectively [44].

Thus, the surface temperature rise (ΔT), the number of pulses (N), and the accumulated temperature rise ($T = N \cdot \Delta T$) are calculated to be 0.00315 K , 15 , 0.0472 K at the laser power of 6 mW from Equations (4.25), (4.26), and (4.27), respectively.

As the accumulated temperature rise ($T = 0.0472 \text{ K}$) is far lower than the required temperature range ($1000\text{-}1600 \text{ K}$) for thermal oxidation in literatures, it can be deduced that laser-induced non-thermal oxidation phenomenon is responsible for Si surface oxidation and formation of the swelled oxide lines.

Based on the accumulated temperature rise at the incident power of 6 mW , we attribute swelling to the onset of localized non-thermal oxidation. Figure 4.26 illustrates the microscopic mechanism of the laser-induced oxidation (photothermal oxidation). For photon energies ($E_{\lambda = 775 \text{ nm}} = 1.6 \text{ eV}$) higher than Si bandgap (1.12 eV), the enhanced oxidation rate is proposed to be due to the electrons excited from Si into the Si-SiO₂ interface. This causes the electrons transferred from Si to adsorb O₂ and enhances the diffusion of O₂ through the oxide layer [44], as shown in Fig. 4.26. Therefore, electron tunneling and O₂ diffusion may explain the initial rapid oxidation.

The emitted electrons could combine with dissolved O₂ in the SiO₂ layer to form O₂⁻. As a result, the concentration of O₂ decreases, while that of O₂⁻ increases. Diffusion of O₂⁻ is also enhanced by the electric field related to the positively charged holes at the Si surface. In the layer near to Si-SiO₂ interface, diffusion of O₂⁻ and O₂ becomes blocked due to lattice mismatch. However, hot electrons emitted into the SiO₂ can easily penetrate the blocking layer and enhance the oxidation rate.

It is also shown in [157, 158] that the photonic enhancement of oxidation is also proportional to the incident photon flux ($F = (I/hc) \cdot \lambda$) during the reaction rather than the power density (I). It implies that the power of 6 mW

would likely suffice to generate adequate number of electron-hole pairs at the Si/SiO₂ interface to trigger the non-thermal oxidation. Deposited photon flux also induces some thermal effect. When the power density increases, more heating of Si surface would occur and eventually wash out the photonic effect and cause excessive surface melting and ablation. This was indeed found to be the case.

Figure 4.26 Microscopic model for the laser-induced surface oxidation.

Potential industrial applications of this process could be (i) micro/nano-device applications, (ii) selective and fast local oxidation, and (iii) debris free marking of Si wafers.

4.5. Magnetic Field Assisted Laser Ablation

4.5.1. Introduction

The use of a magnetic field with laser produced plasma (LPP) is of great interest since a magnetic field can be used to effectively control the dynamic properties of this transient and energetic plasma. The presence of a magnetic field during the expansion of a LPP may initiate several interesting physical

phenomena including conversion of the plasma thermal energy into kinetic energy, plume confinement, ion acceleration, emission enhancement, plasma instabilities, etc[159-166].

Besides its basic research importance, the effect of a magnetic field on the expansion dynamics of LPP has also gained importance in applied research. Regarding to this fact, magnetic confining and steering a LPP have been mostly conducted on pulsed laser deposition (PLD) techniques to get the particulate-free deposition. The effectiveness of debris reduction using magnetically guided PLD has been demonstrated in [167, 168]. Curved solenoid magnetic field of moderate strength (≈ 100 mT) has been used to steer the plasma around the curved arc to the deposition substrate. As a result, a significant reduction in large particulates was observed. Permanent magnets have been also used to deflect and steer the LPP to obtain droplet-free deposition [118, 169, 170].

Although LPP could influence the efficiency of the laser energy-matter coupling through the plasma shielding effect; however, properly adjusting the repetition rate of the pulses could avoid the laser beam-plasma interaction so the plasma shielding effect. Thus, the magnetically confined hot LPP could be used as a secondary energy source to ablate materials.

The effect of an external electric field on Si LPP in order to get debris free surfaces was well studied [26]; hardly any studies can be found in the public domain on magnetized laser micromachining of materials and its effect on ablation rate.

In the present study, we studied the magnetic field-assisted confinement of LPP of silicon, austenitic stainless steel 304 and titanium alloy (Ti4Al6V) and the field effect on ablation rate by introducing an axial magnetic field ($B \perp$ target plane). Magnetohydrodynamic analysis showed that the charged particles in the plasma cloud would be confined to the denser and hotter plasma resulting in plasma heating and enhanced ablation rate.

4.5.2. Materials and Experimental Method

The materials used in the study were silicon wafer (100), austenitic stainless steel, and titanium alloy (Ti4Al6V). Silicon wafer (100) was a single crystal n-type (phosphorous doped) with a resistivity $\rho=1-20 \text{ } \Omega \cdot \text{cm}$ and thickness of 300 μm . The wafer was cut into $10 \times 10 \text{ mm}^2$ pieces. Ultrasonic cleaning of the samples was carried out in methanol for 10 min, acetone for another 10 min, and then de-ionized water for 30 min. Stainless steel and titanium alloy were cut into $20 \times 20 \text{ mm}^2$ pieces and polished with the sandpapers of No. 180, 400, 800, and 1200.

The laser used was the Coherent Avia X10W Q-switched DPSS UV laser system with wavelength $\lambda = 355 \text{ nm}$, frequency $f = 1 \text{ kHz}$, and the pulse width $\approx 20 \text{ ns}$. The output beam profile was Gaussian shape. The spatial mode was TEM00 ($M^2 < 1.3$). The beam divergence was less than 0.3 mrad. The laser beam was introduced to the sample surface using a galvanometric scanner with an f-theta flat field lens with focal length of 100 mm. The galvanometric scanner was used to control the laser beam via the PC. The scanning speed could be set at up to 2000 mm/s. The scanning speed was set at 1 mm/s. Working frequency of the laser machine is fixed at 1 kHz and we aimed to deliver the laser pulses as many as possible into the laser spot to accumulate laser energy in order to make Si oxidation happen. Thus we have chosen the minimum scanning speed of 1 mm/s to achieve the aim.

Ti-sapphire femtosecond laser system (Clark-MXR, CPA 2001) was also used to irradiate silicon samples. The laser has wavelength $\lambda = 775 \text{ nm}$, pulse duration $\tau_l = 150 \text{ fs}$, and pulse repetition rate $f = 1 \text{ kHz}$. IDI LASER scanning system was used to scan the surface. The laser experiments were carried out in ambient at a fixed scanning speed of 1 mm/s with various laser powers (6, 10, 20, 50 mW). A lens of 100 mm focal length was used to focus the laser beam.

The magnetic field for this experiment was produced by a 385-turn copper coil of 60 mm inner diameter, with a current (20 – 150 Ampere) passing

through it, as shown in Figure 4.27. This coil system was made of copper wire with diameter of 3.5 mm. It can produce a uniform magnetic field 0.05 - 0.4 T over 50 mm along its axis at the center. The direction of magnetic field (upward or downward) can be adjusted by the direction of current passing through the coil. DC arc welding machine was used as power supply. Ampere meter was used to measure the current supplied to the coil. The digital thermometer was used to check the temperature of the coil during operation. The electrical fan was also used for cooling the coil.

Figure 4.27 Experimental setup of magnetic-assisted laser ablation of Si

The samples irradiated at various laser powers and magnetic field strength were observed by scanning electron microscope (SEM) and confocal microscope.

4.5.3. Magnetic Field Assisted Nanosecond Laser Ablation – Results and Discussion

Silicon surface was irradiated using various laser energies (35, 56, and 112 μJ) under the different field conditions:

- (1) no magnetic field,
- (2) with magnetic field downward (0.192 T ↓ and 0.341 T ↓), and
- (3) with magnetic field upward (0.341 T ↑).

Two schemes of irradiation were chosen line irradiation scheme and pocket irradiation scheme. The irradiation was conducted with scanning speed 1 mm/s and the surfaces were characterized by scanning electron microscope and confocal microscope.

Firstly, the irradiation was conducted in line scheme. The typical results are shown in Figures 4.28, 4.29, 4.30, 4.31, and 4.32.

The surface was irradiated using the laser energy of 35 μJ in the field free ambient in which the surface is not subjected to any external magnetic field. The observation revealed that almost no ablation occurred, as shown in Figure 4.28(a). Figure 4.29(a) shows the profile of the irradiated line that is very shallow crater with 100 nm depth. The field was increased to 0.192 T downward and applied during the irradiation. It is very interesting to observe that the irradiated line was ablated much deeper with more deposition at the rim comparing with no field one, as shown in Figure 4.28(b). Depth of the crater was observed to be about 1.8 μm , as the profile shown in Figure 4.29(b). The results indicate great influence of the field on ablation threshold. It obviously decreases the ablation threshold. So, we further increased the field strength to 0.341 T downward and ablation depth was found to be deeper with 9.8 μm depth, as shown in Figure 4.28(c) and Figure 4.29(c). The irradiated line was observed that is not straight, as seen in Figure 4.28(c). Presumably, that would be due to laser-produced plasma and the magnetic field interactions. Also, we attributed deeper ablation depth to the plasma confinement under the influence of external magnetic field that will be explained in details. Finally, the surface was subjected to the same field strength (0.341 T) but upward, i.e. it faces out of the surface. The observation showed nearly same ablation trend with ablation depth 9.7 μm but with more deposition layer at the rim comparing with that of in downward field, as shown in Figure 4.28(d) and Figure 4.29(d).

Figure 4.28 SEM images of Si surface irradiated in line scheme using the laser energy $35\ \mu\text{J}$ in various magnetic field conditions (a) no field, (b) $0.192\ \text{T}$ downward field, and (c) $0.341\ \text{T}$ downward field, and (d) $0.341\ \text{T}$ upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Figure 4.29 Profile of the Si surface irradiated using the laser energy of 35 μJ in various field strength and direction (a) no field, (b) 0.192 T downward field, (c) 0.341 T downward field, and (d) 0.341 T upward field. Insets are the image from confocal microscope. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Since the laser energy enhances the density and temperature of laser-produced plasma in a way that can affect the plasma properties, we increased the laser energy to 56 μJ with the same field conditions (0, 0.192 T $\downarrow$, 0.341 T $\downarrow$, 0.341 T $\uparrow$). The surface irradiated with the laser energy 56 μJ under no external field was found to be ablated with depth of 1.5 μm and massive deposition at the rim, as shown in Figure 4.30(a) and Figure 4.31(a). The field was increased to 0.192 T downward during the irradiation resulting in the ablation of 5.4 μm depth with coarse edges, as shown in Figure 4.30(b) and Figure 31(b). The field was further increased to 0.341 T downward and applied during the irradiation. The surface observation showed the deeper ablated crater of 14.1 μm depth, as shown in Figure 4.30(c) and Figure 4.31(c). In the attempt

to realize the influence of the field direction, the field of 0.341 T upward was applied with the same irradiation condition. The observation showed the crater of 14 μm depth that is the same as the one in the field of 0.341 T downward, as shown in Figure 4.30(d) and Figure 4.31(d).

Figure 4.30 SEM images of Si surface irradiated in line scheme using the laser energy 56 μJ in various magnetic field conditions (a) no field, (b) 0.192 T downward field, and (c) 0.341 T downward field, and (d) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Figure 4.31 Profile of the Si surface irradiated using the laser energy of 56 μJ in various field strength and direction (a) no field, (b) 0.192 T downward field, (c) 0.341 T downward field, and (d) 0.341 T upward field. Insets are the image from confocal microscope. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

It can be easily notified that the greater efficiency in ablation is brought about by the magnetic field.

The surface further was irradiated in line scheme using greater laser energy of 112 μJ and characterized by SEM. At the beginning, the surface was irradiated under no external field that the result shows coarse edges and shallow ablation depth, as shown in Figure 4.32(a). Alike previous laser experiments, the field of 0.912 T downward was also applied at the laser energy 112 μJ that leads into deeper ablation with relatively sharp and clean rim, as shown in Figure 4.32(b). This indicates that applying external magnetic could result in not only deeper ablation but also clean rim which might be due to the more concentrated energy and effective evaporation of the removed material. The surface was also irradiated under the field 0.341 T downward and upward, as

shown in Figure 4.32(c) and 4.32(d). The surface irradiated under the field 0.341 T downward consists of granular grains along the ablation region, as shown in Figure 4.32(c). It might be the result of interaction between the silicon surface and ablation plume under the magnetic field. The surface irradiated in the field 0.341 T upward shows the same trend as the one in the field 0.341 T downward, as shown in Figure 4.32(d). The profile of the irradiated line using the laser energy 112 μJ could not be obtained by confocal microscope due to being so deep.

The laser micromachining with magnetic field so far has showed very promising results, particularly when the magnetic field strength increases.

Figure 4.32 SEM images of Si surface irradiated in line scheme using the laser energy 112 μJ in various magnetic field conditions (a) no field, (b) 0.192 T downward field, and (c) 0.341 T downward field, and (d) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Next, we selected the second irradiation scheme where silicon surface was irradiated in a pocket fashion to evaluate capability of the method for laser milling (volume material removal). The pocket of $0.5 \times 0.5 \text{ mm}^2$ was chosen to be irradiated under the influence of magnetic field. The scanning pitch and speed were set at $10 \text{ }\mu\text{m}$ and 1 mm/s . Alike the linear irradiation scheme, various laser energies (35, 56, and $112 \text{ }\mu\text{J}$) were chosen to irradiate the surface in different magnetic field conditions (0 , $0.192 \text{ T } \downarrow$, $0.341 \text{ T } \downarrow$, and $0.341 \text{ T } \uparrow$). The typical results are shown in Figures 4.33, 4.34, 4.35, 4.36, 4.37, and 4.38.

Silicon surface was initially irradiated with the laser energy of $35 \text{ }\mu\text{J}$ in air under no field condition. No ablation occurred on the surface except being wavy due to the laser-surface interaction, as shown in Figure 4.33(a) and Figure 4.34(a). However, when the same irradiation was carried out under the field of 0.192 T downward, the surface was ablated as rough cavity with average depth of $5 \text{ }\mu\text{m}$, as shown in Figure 4.33(b) and Figure 4.34(b). This indicates remarkable decrease in the ablation threshold under the influence of the magnetic field.

The field was further increased to $0.341 \text{ T } \downarrow$ and applied on the surface. The results showed the deeper ablated cavity with about $18 \text{ }\mu\text{m}$ depth, as shown in Figure 4.33(c) and Figure 4.34(c). Later, the field with same magnitude but with opposite direction ($0.341 \text{ T } \uparrow$) was applied during the irradiation. The observation revealed the ablated cavity is the same as the one ablated under $0.341 \text{ T } \downarrow$ but rougher, Figure 4.33(d) and Figure 4.34(d).

Figure 4.33 SEM images of Si surface irradiated in pocket scheme using the laser energy 35 μJ in various magnetic field conditions (a) no field, (b) 0.192 T downward field, and (c) 0.341 T downward field, and (d) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Figure 4.34 Profile of Si surface irradiated in pocket scheme using the laser energy 35 μJ in various magnetic field conditions (a) no field, (b) 0.192 T downward field, and (c) 0.341 T downward field, and (d) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

The laser energy was increased to 56 μJ and used to irradiate the silicon surface. The surface was initially irradiated in air under no field condition. The irradiated area was ablated as shallow cavity of about 5 μm depth, as shown in Figure 4.35(a) and Figure 4.36(a). When the same irradiation was conducted under the field of 0.192 T $\downarrow$, the surface was ablated deeper with average depth of 15 μm , as shown in Figure 4.35(b) and Figure 4.36(b). The field was further increased to 0.341 T $\downarrow$ and applied on the surface. The results showed the much deeper ablated cavity with about 50 μm depth, as shown in Figure 4.35(c) and Figure 4.36(c). This indicates that the field strength has crucial influence on the ablation depth. Later, the field with same magnitude but with opposite direction (0.341 T $\uparrow$) was applied during the irradiation. The observation showed the same ablated cavity as the one ablated under 0.341 T $\downarrow$ but rougher, Figure

4.35(d) and Figure 4.36(d). It is deduced that the polarity of the field does not has considerable influence on the ablation depth.

Figure 4.35 SEM images of Si surface irradiated in pocket scheme using the laser energy 56 μJ in various magnetic field conditions (a) no field, (b) 0.192 T downward field, and (c) 0.341 T downward field, and (d) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Figure 4.36 Profile of Si surface irradiated in pocket scheme using the laser energy $56 \mu\text{J}$ in various magnetic field conditions (a) no field, (b) 0.192 T downward field, and (c) 0.341 T downward field, and (d) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Furthermore, the laser energy was increased to $112 \mu\text{J}$ and used to irradiate the surface under various field conditions (0 , $0.192 \text{ T} \downarrow$, $0.341 \text{ T} \downarrow$, and $0.341 \text{ T} \uparrow$) as before. The surface irradiated under no field was found to be ablated as cavity with about $40 \mu\text{m}$ depth, as shown in Figure 4.37(a) and Figure 4.38(b). However, interestingly the field $0.192 \text{ T} \downarrow$ enhanced the ablation depth to about $150 \mu\text{m}$ that is 3 times more than the field free one, as shown in Figure 4.37(b) and Figure 4.38(b).

When the field was further increased to $0.341 \text{ T} \downarrow$, the ablated cavity was found to be much deeper about $204 \mu\text{m}$ depth, as shown in Figure 4.37(c) and Figure 4.38(c). The effect of upward field was also examined. It resulted into

the ablation depth of about 200 μm , as shown in Figure 4.37(d) and Figure 4.38(d).

Figure 4.37 SEM images of Si surface irradiated in pocket scheme using the laser energy 112 μJ in various magnetic field conditions (a) no field, (b) 0.192 T downward field, and (c) 0.341 T downward field, and (d) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Figure 4.38 Profile of Si surface irradiated in pocket scheme using the laser energy 112 μJ in various magnetic field conditions (a) no field, (b) 0.192 T downward field, and (c) 0.341 T downward field, and (d) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

As laser-induced plasma properties depends on the material under the irradiation, we decided to irradiate different materials (stainless steel and titanium alloy) under the influence of magnetic field.

Stainless steel (SS) surface was irradiated in line fashion with scanning speed of 1 mm/s using laser energy 112 μJ and under various field conditions (0, 0.341 T $\downarrow$, and 0.341 T $\uparrow$). The results are shown in Figure 4.39 and Figure 4.40.

Firstly, the surface was irradiated in air under no field condition and found to be ablated as shallow line with about 13 μm depth and 38 μm diameter, as shown in Figure 4.39(a) and Figure 4.40(a). However, when the field of 0.341 T $\downarrow$ was applied during the irradiation, it is observed that the ablated line is deeper

with about 35 μm depth and narrower with about 23 μm width comparing with the one done in the field free condition, as shown Figure 4.39(b) and Figure 4.40(b). The laser experiment was followed by applying the field with the same magnitude but opposite direction (0.341 T $\uparrow$). The irradiated line was found to be ablated as crater with about 25 μm depth and 20 μm width, as shown in Figure 4.39(c) and Figure 4.40(c). The results revealed that under the downward magnetic field the ablated trace becomes deeper comparing with one done under the upward field. This indicates that the field polarity has influence on the ablation depth when the stainless steel surface is irradiated, while such behavior was not observed during Si surface irradiation.

Figure 4.39 SEM images of stainless steel surface irradiated in line scheme using the laser energy 112 μJ in various magnetic field conditions (a) no field, (b) 0.341 T downward field, and (c) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Figure 4.40 Profile of stainless steel surface irradiated in line scheme using the laser energy 112 μJ in various magnetic field conditions (a) no field, (b) 0.341 T downward field, and (c) 0.341 T upward field. $\downarrow$ and $\uparrow$ indicate downward and upward field direction, respectively.

Titanium alloy (Ti4Al6V) surface was also irradiated in pocket fashion with scanning pitch and speed of 10 μm and 1 mm/s using laser energy 112 μJ under two conditions without and with the magnetic field (0, 0.341 T $\downarrow$). Initially the surface was observed using optical microscope as shown in Figure 4.41. Figure 4.41(a) shows the slightly color change at the irradiated area under the influence of no magnetic field. It seems that the surface is not ablated considerably. However, when the surface irradiated under the magnetic field of 0.341 T $\downarrow$ was observed, it was found to be darker, as shown in Figure 4.41(b). It might be due to the excessive surface ablation. Thus we used SEM to have closer look at the surface.

Closer look at the surface irradiated under no field revealed that the ablation occurs and roughens the surface with no considerable material removal, as shown in Figure 4.42(a). However, Figure 4.42(b) shows the excessive ablation of the surface irradiated under 0.341 T $\downarrow$ that is rougher with more deposition of the abated materials. This makes the surface looks optically darker, as shown in Figure 4.41(b).

Figure 4.41 Optical microscope images of Ti alloy surface irradiated in pocket scheme using the laser energy 112 μJ in two conditions (a) no field, (b) 0.341 T downward field. $\downarrow$ indicates downward field direction, respectively.

Figure 4.42 SEM images of Ti alloy surface irradiated in pocket scheme using the laser energy 112 μJ in two conditions (a) no field, (b) 0.341 T downward field. $\downarrow$ indicates downward field direction, respectively.

4.5.4. Magnetic Field Assisted Femtosecond Laser Ablation – Results and Discussion

Silicon surface was irradiated using various laser powers (6, 10, 20, 50 mW) under two different conditions:

- (1) no magnetic field, and
- (2) with magnetic field downward (0.341 T ↓).

Two schemes of irradiation were chosen line irradiation scheme and pocket irradiation scheme. The irradiation was conducted with scanning speed 1 mm/s and the surfaces were characterized by scanning electron microscope and confocal microscope.

The results are shown in Figure 4.43(a)-(h). No discernible change was found on surface irradiated using the lowest power of 6 mW in both irradiation conditions (no field and 0.341 T ↓), as shown in Figure 4.43(a)-(b) and Figure 4.44(a)-(b).

At the laser power of 10 mW, the surface irradiated in no field condition was found to be oxidized in some locations and rose 0.75 μm above the original surface, as shown in Figure 4.43(c) and Figure 4.44(c). This indicates that the laser energy is just about the energy required to oxidize the surface. Fluctuation of the laser power is cause of discontinuous oxidation. Same laser power (10 mW) was used to irradiate the surface under the influence of the magnetic field 0.341 T ↓. The surface was found to be oxidized completely under the magnetic field and rose 1 μm above the original surface, as shown in Figure 4.43(d) and Figure 4.44(d). This indicates that applying magnetic field overheats the surface and overcomes the power fluctuation to make the oxidation occurred on the surface continuously.

Figure 4.43 SEM images of Si surface irradiated in line using fs laser with various laser powers in different conditions (a) 6 mW, no field, (b) 6 mW, 0.341 T ↓, (c) 10 mW, no field, (d) 10 mW, 0.341 T ↓, (e) 20 mW, no field, (f) 20 mW, 0.341 T ↓, (g) 50 mW, no field, and (h) 50 mW, 0.341 T ↓. ↓ indicates downward field direction.

Figure 4.44 Profile of Si surface irradiated in line using fs laser with various laser powers in different conditions (a) 6 mW, no field, (b) 6 mW, 0.341 T ↓, (c) 10 mW, no field, (d) 10 mW, 0.341 T ↓, (e) 20 mW, no field, (f) 20 mW, 0.341 T ↓, (g) 50 mW, no field, and (h) 50 mW, 0.341 T ↓. ↓ indicates downward field direction.

When the laser power 20 mW was used to irradiate the surface in no field condition, the surface was found to be ablated with 1.5 μm depth, as shown in Figure 4.43(e) and Figure 4.44(e). However, when the same power (20 mW) was used under 0.341 T $\downarrow$, the ablation depth was slightly increased to 1.8 μm , as shown in Figure 4.43(f) and Figure 4.44(f). It is deduced that despite the great effect of the magnetic field on nanosecond laser ablation it does not cause big change in ablation when the surface is irradiated using femtosecond laser.

At the highest laser power of 50 mW, the irradiated surfaces were found to be ablated in same trend but with little difference in ablation depth, 2.3 μm in no field condition and 2.5 μm in 0.341 T $\downarrow$, as shown in Figure 4.43(g)-(h) and Figure 4.44(g)-(h).

Next, we selected the second irradiation scheme where silicon surface was irradiated in a pocket fashion to evaluate capability of the method for femtosecond laser milling (volume material removal). The pocket of $0.2 \times 0.2 \text{ mm}^2$ was chosen to be irradiated under the influence of the magnetic field. The scanning pitch and speed were set at 10 μm and 1 mm/s. Like the linear irradiation scheme, various laser powers (6, 10, 20, and 50 mW) were chosen to irradiate the surface under two conditions (no field and 0.341 T $\downarrow$). The typical results are shown in Figure 4.45.

Silicon surface was initially irradiated with the laser power of 6 mW in air under no field condition. The observation showed that the surface is oxidized in very few places, as shown in Figure 4.45(a). This is due to overlapping the irradiation spots that provides enough energy to activate the surface oxidation while such oxidation was not observed in line irradiation, see Figure 4.43(a). The irradiation was also conducted under influence of 0.341 T $\downarrow$. The surface oxidation occurred in more places comparing with no field one, as shown in Figure 4.45(b).

When the surface was irradiated using the laser power of 10 mW, it is found that the surface is completely oxidized under both conditions, no field and 0.341 T $\downarrow$, as shown Figure 4.45(c) and Figure 4.45(d).

However, when the irradiation was carried out using the laser power 20 mW, the surface was found to be ablated as rough cavity in both conditions (no field and 0.341 T $\downarrow$) with nearly the same ablation trend as the one in line irradiation, as shown in Figure 4.45(e) and Figure 4.45(f). The same situation of ablation was also observed for the laser power of 50 mW, as shown in Figure 4.45(g) and Figure 4.45(h). This again shows that the efficiency of applying magnetic field in femtosecond laser ablation is low comparing with that in nanosecond laser ablation. This might be originated from the nature of the induced plasma in fs and ns laser-matter interaction. The plasma in femtosecond laser-matter interaction is highly composed of electrons while in nanosecond laser-matter interaction it is highly compose of ions.

Figure 4.45 SEM images of Si surface irradiated in pocket using fs laser with various laser powers in different conditions (a) 6 mW, no field, (b) 6 mW, 0.341 T ↓, (c) 10 mW, no field, (d) 10 mW, 0.341 T ↓, (e) 20 mW, no field, (f) 20 mW, 0.341 T ↓, (g) 50 mW, no field, and (h) 50 mW, 0.341 T ↓. ↓ indicates downward field direction.

4.5.5. Magnetic Field Assisted Laser Ablation – Analysis

An external magnetic field parallel to the propagation direction of a laser beam will inhibit the diffusion losses of the laser-produced plasma (LPP) and thereby reduce the ablation threshold [171]. LPP could be considered as a fluid and its expansion dynamics can be described by the equations of the fluid dynamics. Applied magnetic field adds the term of Lorentz force ($\mathbf{F}_m = \mathbf{j} \times \mathbf{B}$) into the momentum equation of the plasma, as seen in equation (4.28) [172].

$$\rho \frac{\partial \mathbf{V}}{\partial t} + \rho(\mathbf{V} \cdot \nabla) \mathbf{V} = -\nabla p + \mathbf{j} \times \mathbf{B} + \rho \mathbf{g} \quad (4.28)$$

where $\mathbf{V}$ is the fluid velocity, ρ is the total charge density, p is the fluid pressure, $\mathbf{j}$ is the current density carried by particles, $\mathbf{B}$ is the external magnetic field, and $\mathbf{g}$ is the gravitational acceleration.

Lorentz force provides a link between the fluid equation and electromagnetic equation as equation (4.29), where μ_0 is the permeability of the media.

$$\mathbf{F}_m = \mathbf{j} \times \mathbf{B} = \frac{1}{\mu_0} (\nabla \times \mathbf{B}) \times \mathbf{B} \quad (4.29)$$

Equation (4.29) can be simplified using Equation (4.30):

$$\nabla \left(\frac{1}{2} \mathbf{B} \cdot \mathbf{B} \right) = \mathbf{B} \times (\nabla \times \mathbf{B}) + (\mathbf{B} \cdot \nabla) \mathbf{B} \quad (4.30)$$

Thus Equation (4.29) can be written as Equation (4.31).

$$\mathbf{F}_m = \frac{1}{\mu_0} (\mathbf{B} \cdot \nabla) \mathbf{B} - \nabla \left(\frac{B^2}{2\mu_0} \right) = \nabla \left(\frac{\mathbf{B}\mathbf{B}}{\mu_0} - \frac{B^2}{2\mu_0} \mathbf{I} \right) = \nabla \cdot \mathbf{M} \quad (4.31)$$

$\mathbf{M}$ is the Maxwell stress tensor with the following definition, with the magnetic field parallel to the direction of the beam propagation (normal to the target surface), it will be in the form of Equation (4.32).

$$\mathbf{M} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & T_m \end{bmatrix} - \begin{bmatrix} p_m & 0 & 0 \\ 0 & p_m & 0 \\ 0 & 0 & p_m \end{bmatrix} \quad (4.32)$$

where T_m is the magnetic tension, and p_m is the magnetic pressure.

Lorentz force ($\mathbf{F}_m$) has as two terms. The former is the magnetic tension ($T_m = B^2/\mu_0$) which depends on the direction of the applied magnetic field. The latter is the magnetic pressure ($p_m = B^2/2\mu_0$) per unit area which is isotropic and independent from the field direction. This indicates that the magnetic field acts like a pressure in the directions transverse to $\mathbf{B}$ and like a tension in the direction of parallel to $\mathbf{B}$.

Since the applied magnetic field was aligned with the z-axis ($\mathbf{B} = \pm (0.341)\mathbf{k}$), it slows down the expansion of the LPP and prevents the rapid decrease in the electron density and temperature, as seen in Figure 4.46. Figure 4.46(a) shows the plasma under no field condition. The isotropic magnetic pressure ($p_m = B^2/2\mu_0$) confines LPP and rises the collisional ionization of neutral species through a confinement of electrons and ions [173]. It might be responsible for the high density and hot plasma resulting to the plasma heating and lowering the ablation threshold. Beside the isotropic magnetic pressure, the downward magnetic field also applies the axial magnetic compression (

$\sigma_m = B^2/\mu_0$), as shown in Figure 4.46(b). It pushes the LPP down towards the laser spot causing more plasma heating effect.

However, when the field direction is changed to the upward one it applies the axial magnetic tension ($T_m = B^2/\mu_0$), as shown in Figure 4.46(c). It stretches the LPP a little away from laser spot. Therefore, it may explain the slight difference of the ablation depth in the downward and upward magnetic field.

Figure 4.46 Laser produced plasma (LPP) expansion and the influence of the magnetic field in various conditions: (a) without magnetic field, (b) with downward magnetic field, and (c) with upward magnetic field.

Although the analysis shows the confinement effect of the magnetic field on the induced plasmas, however, the results showed that laser ablation efficiency in fs laser irradiation is lower than that in ns laser irradiation. Since the induced plasma properties in fs and ns irradiation are different, this could result in different laser ablation efficiency.

Fs-induced plasma is dominated mostly by electrons cloud rather than ions/atoms/particles cloud in ns-induced plasma. It is well known that thermal

capacity of electrons is much lower than that of ions/atoms/particles. Thus it could be deduced that thermal energy being stored in fs-induced plasma is lower than that in ns-induced plasma. This causes quick thermal dispersion in fs-induced plasmas.

On the other hand, the temperature and electron number density of fs-induced plasmas decrease faster than in ns-induced plasmas due to different energy deposition mechanism [174]. This is because of no laser-plasma interactions in the fs irradiation. The plasma cools quickly since no further energy is supplied by the fs laser. This is why the enhancement of ablation in fs laser ablation is lower than ns laser ablation.

However, a fraction of the laser energy is absorbed by the ns-induced plasma that results in greater temperature and electron density. Thus the ns-induced plasma is denser and hotter comparing the fs-induced plasma and it becomes more dense and hot under the influence of the external magnetic field. This leads to efficient plasma heating and high laser ablation efficiency in ns laser ablation, as shown in the results.

It should be noted that the efficiency of laser-material interaction is mostly affected by the existence of a plasma above the substrate. Under proper conditions the plasma is responsible for the major and rapid heat input to the substrate. In some conditions, the laser induced plasma acts on the negative way when the plasma density is above critical value causing inverse Bremsstrahlung absorption and refraction of the laser beam.

Using high repetition rate pulsed laser and shorter wavelength are the current techniques which interfere the growth of the plasma.

As stated earlier, in ns-induced plasma, a fraction of the laser energy is absorbed by the plasma that results in greater temperature and electron density. It may cause plasma energy re-deposition to the workpiece and enhanced ablation. This may also cause thermal lateral damages to the substrate specially high thermal conductive material such as stainless steel and Ti alloy. This needs further investigation.

It is also possible for the plasma to act as a dielectric waveguide for the laser radiation. This effect, sometimes known as “beam-trapping [175]. This also requires further investigation.

In this study, we proposed the magnetic field-assisted laser ablation enhancement of the materials using an axial magnetic field. Theoretical analysis based on magnetohydrodynamic (MHD) has been conducted. It explains that the ablation enhancement could be due to magnetic field confinement of the plasma and plasma heating of the target surface. It is expected that this technique would have potential applications in the laser processing of hard-to-ablate materials, laser cutting, laser welding, etc.

Chapter 5: Conclusions and Future Directions

5.1. Conclusions

We investigated various research areas in this thesis, including: laser micromachining of silicon using infrared fiber laser ($\lambda = 1090$ nm), non-ablative thermal texturing, non-ablative non-thermal texturing, and laser ablation under the influence of the external magnetic field.

We studied and analyzed laser micromachining of silicon using infrared fiber laser ($\lambda = 1090$ nm). The results showed that the infrared fiber laser could not be regarded as a suitable tool for laser micromachining of silicon. The absorption analysis revealed that silicon is highly transparent to the infrared wavelength of fiber laser ($\lambda = 1090$ nm) thus the laser beam goes through the silicon before get absorbed and ablate the material. This indicates that absorption coefficient is of great importance in laser processing of materials.

Characterization of the irradiated surface revealed the formation of raised volumes of silicon and silicon oxide at the rim of the shallow kerfs. It was proposed that the oxidation induced by fiber laser could be used to produce regularly-patterned surfaces. To this aim, Si surfaces instead of being irradiated for the purpose of machining were irradiated below the ablation threshold in various environments to enhance oxidation and make a use of that for the texturing purpose.

Laser-based surface texturing is mainly based on the target ablation and redistribution of melt materials. Hardly any reports can be found in the public domain on use of non-ablative laser surface texturing to form uniform micro-bumps. Silicon is known as highly transparent to the infrared fiber laser, so it is not considered as a suitable tool for ablative texturing of silicon. Thus, we investigated the non-ablative laser surface texturing of silicon and succeeded in fabricating regular arrays of submicron bumps on silicon surface through non-ablative texturing with CW fiber laser.

The bumps were found to be SiO₂ based on EDX analysis. Formation of the bumps was explained qualitatively by laser-induced localized Si oxidation. Potential applications of this process are: (i) flexible, selective and fast local rapid thermal oxidation, (ii) debris-free wafer marking and SiO₂ structures for optical uses, and (iii) surface textures for new surface functionality.

We investigated the formation mechanism of the bumps quantitatively through finite element method. The non-ablative surface texturing was explained in terms of laser-induced localized thermal oxidation [15]. However, the proposed mechanism is based on qualitative analyses only. Thus, we used finite element method to gain better understanding of the non-ablative texturing mechanism. It is found that the bumps formation is due to the laser-induced localized Si oxidation.

The map of laser parameters (laser power and dwell time) was prepared using simulation results to represent the Si surface effective oxidation zone. It may be used to optimize the laser parameters leading to stable growth of Si oxide and uniform formation of bumps on the Si surface.

We also investigated non-ablative non-thermal laser surface texturing. Non-ablative laser surface texturing could be based on either thermal or non-thermal mechanism. Few works have been just reported on non-ablative laser surface texturing of silicon which are thermal basis, using CW fiber laser [15] or high repetition rate (MHz) femtosecond laser pulses [153] to accumulate thermal effects for thermally induced non-ablative texturing. However, the surface was irradiated using low repetition rate (1 kHz) of femtosecond laser pulses and we succeeded in non-ablative non-thermal direct writing of silicon surface.

The swelled lines were found to be SiO₂ based on EDX and Raman spectroscopy analyses. Since the surface was irradiated using a low repetition rate (1 kHz) of femtosecond pulsed laser with negligible heat accumulation, formation of the lines was explained qualitatively by laser-induced non-thermal Si oxidation. Thermal analysis of the irradiated line was also conducted that

indicates the temperature is below the thermal oxidation zone. This provides evidence that the formation mechanism might be based the non-thermal characteristic. Potential applications of this process are also could be (i) micro/nano-device applications, (ii) selective and fast local oxidation, and (iii) debris free marking of Si wafers.

We investigated laser ablation of materials under the influence of external magnetic field. The use of magnetic field with laser produced plasma (LPP) is of great interest in science and engineering field since magnetic field could effectively control the dynamic properties of this transient and energetic plasma. Beside its basic research importance, magnetic field has been widely used in engineering research including pulsed laser deposition (PLD) to get the particulate-free deposition. However, hardly any report can be found in public domain on magnetized laser micromachining of materials and its effect on ablation rate.

Thus we studied the magnetic field-assisted ns and fs laser ablation of silicon, stainless steel, and titanium alloy (Ti4Al6V) by introducing an axial magnetic field ($B \perp$ target plane). Firstly, the surfaces were irradiated using nanosecond laser (355 nm, 20 ns) in line and pocket schemes. SEM and the profile images showed very high laser ablation efficiency. Later, fs laser (775 nm, 150 fs) was used to irradiate silicon surface. It is found that laser ablation efficiency in fs laser is lower comparing that in ns laser. Since the induced plasma properties in fs and ns irradiation are different, so this could result in different laser ablation efficiency. The temperature and electron number density of fs-induced plasmas decreases faster than ns-induced plasmas due to different energy deposition mechanism [174]. This is because of no laser-plasma interactions in the fs irradiation. The plasma cools quickly since no further energy is supplied by the fs laser. However, a fraction of the laser energy is absorbed by the ns-induced plasma that results in greater temperature and electron density.

Magnetohydrodynamic (MHD) analysis showed that the magnetic field confines the induced plasmas. Thus the ns-induced plasma that is denser and hotter comparing the fs-induced plasma becomes more dense and hot under the influence of the external magnetic field. This leads to efficient plasma heating and high laser ablation efficiency in ns laser ablation, as shown in the results.

It is expected that this technique would have potential applications in the laser processing of hard-to-ablate materials, laser cutting, laser welding, etc.

5.2. Novelty and Major contributions

(1) Non-ablative surface texturing:

Surface texturing is an important research area with a broad range of applications. The laser ablation-based surface texturing has been well studied. Hardly any reports can be found in the public domain on use of non-ablative laser surface texturing to form uniform micro-bumps. We have developed non-ablative methods based on "laser-induced thermal and non-thermal oxidation" to fabricate a regular array of micro-bumps on Si. Potential industrial application of the method could be (i) flexible, selective and fast local rapid thermal/non-thermal oxidation, (ii) debris free wafer marking and SiO₂ structures for optical uses, and (iii) surface textures for new surface functionality.

(2) Surface texturing by magnetic field assisted laser-produced plasma:

Applying a magnetic field on laser produced plasma (LPP) has broad applications in both basic and applied research due to its effect on spatial and temporal dynamics of LPP. Most of attempts in applied research have been conducted in the field of pulsed laser deposition (PLD), laser welding and laser surface hardening, but no studies can be found on magnetic field assisted laser surface texturing and micromachining of materials. We have investigated and developed the novel technique of the magnetic field assisted nanosecond and femtosecond laser micromachining of Si, stainless steel and Ti Alloy with an

axial magnetic field ($B \perp$ target surface). Magnetohydrodynamic (MHD) analysis and experimental results showed successful application of the magnetic field as a tool to confine LPP and to enhance material's ablation efficiency. It is expected to open broad applications in laser material processing.

5.3. Future Directions

Although we have made good progress studying non-ablative texturing of silicon surface, there remain many unanswered questions and exciting avenues of research to explore in non-ablative texturing area. We have just used CW infrared fiber laser ($\lambda = 1090$ nm) in O_2 and femtosecond laser in air.

Research can be done to further understand effects of various laser parameters (wavelength and pulse duration) and irradiation environment on the laser-induced thermal/non-thermal oxidation in silicon and many other materials. This could help to optimize non-ablative texturing of material surfaces.

Regarding to non-thermal oxidation of silicon, much work either experimentally or numerically needs to be done to describe the detailed mechanism. This would help to control the mechanism in order to improve repeatability of the process. Furthermore, much work needs to be conducted regarding to capability of the technique to functionalize material surfaces. Non-ablative texturing becomes good candidate especially in thermally sensitive materials that need to be subjected to less thermal input.

Although applying magnetic field on laser-induced plasma has drawn more attentions in basic and engineering research, it has not studied in the field of laser micromachining, laser welding and laser cutting. We have just conducted research on magnetic field assisted laser ablation of three materials including silicon, stainless steel and titanium alloy using nanosecond UV laser (355 nm, 20ns). The results showed promising influence of the field on ablation enhancement.

This research area is of great interest to enhance the efficiency of laser material processing. As the properties of laser-induced plasma vary with laser parameters (wavelength and pulse duration) and material under the irradiation, great research works could be done systematically on characterization of various plasmas and controlling their dynamics using magnetic field to improve machinability and weldability of materials.

We have developed the experimental setup including the solenoid copper coil (as shown in Figure 4.27) to apply the magnetic field with limited strength ($B \leq 0.4T$) during the laser-matter interaction. The results showed the promising effect of field strength on enhancement of ablation rate. Higher magnetic field resulted in greater ablation rate. Thus developing a setup that allows applying greater magnetic field is of great interest from technology and research point of view. We have designed superconductor electromagnetic lens in order to reach higher field strength. However, we did not fabricate it; so much works can be done in redesign, simulation and fabrication of such superconductor electromagnetic lens with much stronger and focused field at the irradiation spot. The principles design of high temperature (HT) superconductor electromagnetic lens is shown in Figure 5.1. 3D design of the lens is also shown in Figure 5.2.

Figure 5.1 Principle design of HT superconductor electromagnetic lens to confine laser induced plasma

Figure 5.2 3D design of HT electromagnetic lens to confine laser induced plasma

The higher ablation depth under the influence of the magnetic field gives evidence of concentrated energy of laser-induced plasma due to the plasma confinement. This indicates that the method is capable of being used efficiently

in welding and cutting of thick plates due to deep penetration of ablation and melting. Thus it was decided to investigate that the technique could be applied in arc, laser, and hybrid laser-arc welding. Here is our research proposal to magnetized robotic hybrid laser-arc welding due to being considered widely in industry.

As part of technological efforts to enhance productivity and capabilities in welding techniques, hybrid laser-arc welding (HLAW) is aimed at achieving this. Hybrid welding brings laser and arc sources together that the benefits of both welding process are obtained [176-178]. As a result, hybrid welding produces weld pools that are wider than laser welds and deeper than arc welds. The combination of a laser with an arc process is not only to address some of the short comings of the arc welding technology such as shallow penetration but also to enhance productivity and welds quality.

While there seems to be an increase in the implementation of HLAW processes in many fields such as ship building, automotive, vessel fabrication, and pipe welding up to 15 mm thickness, there still remain obstacles to greater utilization. The main limitation rather than equipment cost is physical limitations of the process. As the weld thickness increases, the ability to produce “free formed root weld” is limited. Today this limit is between 12 mm and 15 mm depending on the laser used.

As implementation of the HLAW process is occurring, future research and development is being accomplished for other applications. While it may not be practical to achieve welding of 25 mm thickness in a single pass with an HLAW process today, it may be possible to achieve this with multiple pass welding. Researchers are investigating this approach for pipe line and thick section applications using HLAW for the root pass and with subsequent pass being HLAW or conventional arc welding.

However, implementing single pass HLAW for thick sections is of great interest to avoid drawbacks associated with multiple pass welding. Thus, we are proposing novel technique of magnetic field assisted HLAW to get high

penetration depth of welding. As we have conducted experiments on applying magnetic field on laser-induced plasma, it is approved that applying magnetic field confines the plasma to very high density then makes the plasma very hot at the surface resulting in high temperature at the interface and high ablation rate. It is also expected that applying magnetic field would be able to enhance not only the penetration depth of the welding but also its productivity and capabilities.

In conjunction with technique development, using the robots in HLAW has gained more interest to improve productivity and weld's quality. However, automatic welding is operating differently from manual welding. Automatic welding normally involves high duty cycles and the welding equipment must be able to operate under those conditions.

Thus in the proposed research area, much work needs to be done to develop new generation of robotic HLAW equipped with superconductor electromagnetic lens mounted on robot's arm to enhance productivity, weld quality and the penetration depth for single pass welding. The principle layout of magnetized HLAW is shown in Figure 5.3. Magnetic field could be also applied in arc welding to obtain confined arc and high penetration depth, as shown schematically in Figure 5.4.

Figure 5.3 schematic setup of magnetized robotic hybrid laser-arc welding

Figure 5.4 Principle illustration of the magnetic field effect on the arc.

Publications

Journal:

- (1) **Hamid Farrokhi**, Wei Zhou, Hongyu Zheng, Xincan Wang, Magnetized laser ablation of materials, **Nature Photonics**, (under review Nov- 2013)
- (2) **H. Farrokhi**, Wei Zhou, H. Y. Zheng, H. Yamamoto, Non-ablative marking of silicon surface with femtosecond laser, **Journal of Micromechanics and Microengineering** (under review Nov-2013)
- (3) **Hamid Farrokhi**, Wei Zhou, Hongyu Zheng, Zhongli Li, Numerical Simulation of Non-ablative Laser Texturing of Silicon Surface with a Continuous Wave Fiber Laser, **Journal of Computational and Theoretical nanoscience** 11, 1-5, 2014.
- (4) **H. Farrokhi**, Wei Zhou, H. Y. Zheng, Z. L. Li, Non-ablative texturing of silicon surface with a continuous wave fiber laser, **Optics Express** 20, 23180-23185, 2012.
- (5) S. Pedrammehr, **H. Farrokhi**, A. Khani Sheykh Rajab, S. Pakzad, M. Mahboubkhah, M. M. Ettetfagh and M. H. Sadeghi, Modal Analysis of the Milling Machine Structure through FEM and Experimental Test, **Advanced Materials Research**, 383-390, 6717-6721, 2012.
- (6) **Hamid Farrokhi**, Wei Zhou, Hongyu Zheng, Zhongli Li, Characterization of Silicon Wafer Surface Irradiated with Fiber Laser, **Key Engineering Materials** 447-448, 715-719, 2010.

Conference:

- (1) **H. Farrokhi**, W. Zhou, H. Y. Zheng, and Z. L. Li, Sub-micron texturing of silicon wafer with fiber laser, **Proc. SPIE 7926**, 792607-12, 2011.
- (2) **H. Farrokhi**, W. Zhou, H. Y. Zheng, Silicon surface texturing by forming sub-micron bumps with a CW fiber laser, **euspen 13th** international conference, Berlin 2013.

- (3) **H. Farrokhi**, J. Hou, W. Zhou, H. Y. Zheng, and Z. L. Li, Molten pool temperature measurement in YAG laser ablation using pyrometer” Conference on Micromachining and Microfabrication Process Technology XVII, MOEMS-MEMS **SPIE Photonics West**, San Francisco, California, USA, Jan 2012.

References

1. T.-H. Her, R. J. Finlay, C. Wu, S. Deliwala, and E. Mazur, "Microstructuring of silicon with femtosecond laser pulses," *Appl. Phys. Lett.* **73**, 1673-1675 (1998).
2. V. Zorba, I. Alexandrou, I. Zergioti, A. Manousaki, C. Ducati, A. Neumeister, C. Fotakis, and G. A. J. Amaratunga, "Laser microstructuring of Si surfaces for low-threshold field-electron emission," *Thin Solid Films* **453–454**, 492-495 (2004).
3. V. Zorba, P. Tzanetakis, C. Fotakis, E. Spanakis, E. Stratakis, D. G. Papazoglou, and I. Zergioti, "Silicon electron emitters fabricated by ultraviolet laser pulses," *Appl. Phys. Lett.* **88**, 081103 (2006).
4. P. Simon, and J. Ihlemann, "Ablation of submicron structures on metals and semiconductors by femtosecond UV-laser pulses," *Appl. Surf. Sci.* **109–110**, 25-29 (1997).
5. B. Borchers, J. Bekesi, P. Simon, and J. Ihlemann, "Submicron surface patterning by laser ablation with short UV pulses using a proximity phase mask setup," *J. Appl. Phys.* **107**, 063106-063105 (2010).
6. J. C. Zolper, S. Narayanan, S. R. Wenham, and M. A. Green, "16.7% efficient, laser textured, buried contact polycrystalline silicon solar cell," *Applied Physics Letters* **55**, 2363-2365 (1989).
7. A. Malcolm, and C. Jeffrey, "Optical and electrical properties of laser texturing for high-efficiency solar cells," *Progress in Photovoltaics: Research and Applications* **14**, 225 - 235 (2006).
8. K. N. Barada, C. G. Mool, and W. K. Kurt, "Spontaneous formation of nanospiked microstructures in germanium by femtosecond laser irradiation," *Nanotechnology* **18**, 195302 (2007).
9. B. K. Nayak, M. C. Gupta, and K. W. Kolasinski, "Formation of nano-textured conical microstructures in titanium metal surface by femtosecond laser

- irradiation," *Applied Physics A: Materials Science & Processing* **90**, 399-402 (2008).
10. B. K. Nayak, and M. C. Gupta, "Femtosecond-laser-induced-crystallization and simultaneous formation of light trapping microstructures in thin a-Si:H films," *Applied Physics A: Materials Science & Processing* **89**, 663-666 (2007).
11. X. C. Wang, H. Y. Zheng, C. W. Tan, F. Wang, H. Y. Yu, and K. L. Pey, "Fabrication of silicon nanobump arrays by near-field enhanced laser irradiation," *Applied Physics Letters* **96**, 084101-084103 (2010).
12. G. Wysocki, R. Denk, K. Piglmayer, N. Arnold, and D. Bauerle, "Single-step fabrication of silicon-cone arrays," *Applied Physics Letters* **82**, 692-693 (2003).
13. S. Alok, and et al., "The generation of nano-patterns on a pure silicon wafer in air and argon with sub-diffraction limit nanosecond laser pulses," *Journal of Physics D: Applied Physics* **43**, 145301 (2010).
14. S.-B. Wen, R. Greif, and R. E. Russo, "Background gas effects on the generation of nanopatterns on a pure silicon wafer with multiple femtosecond near field laser ablation," *Applied Physics Letters* **91**, 251113-251113 (2007).
15. H. Farrokhi, W. Zhou, H. Y. Zheng, and Z. L. Li, "Non-ablative texturing of silicon surface with a continuous wave fiber laser," *Opt. Express* **20**, 23180-23185 (2012).
16. H. Farrokhi, W. Zhou, H. Y. Zheng, and Z. Li, "Sub-micron texturing of silicon wafer with fiber laser," M. A. Maher, J.-C. Chiao, and P. J. Resnick, eds. (SPIE, San Francisco, California, USA, 2011), pp. 792607-792612.
17. Y. X. Gan, "Modeling Energy Conversion and Mass Transfer in Top-Down Nanomanufacturing Processes " *J. Comput. Theoret. Nanosci.* **6**, 985-993 (2009).
18. H. Liu, D. Wan, and D. Hu, "Numerical Simulation and Experimental Studies of Surface Topography of Laser Textured Roller " *J. Comput. Theoret. Nanosci.* **5**, 1570-1573 (2008).

19. X. Ji, J. Zhou, H. Guo, and S. Jiang, "3D Finite Element Simulation for the Temperature Field of Direct Metal Laser Sintering Process " J. Comput. Theoret. Nanosci. **5**, 1578-1582 (2008).
20. X. Yang, X. Jin, and N. Yang, "Numerical Simulation of the Concentration Field of Powder Stream in Coaxial Laser Cladding," J. Comput. Theoret. Nanosci. **5**, 1517-1521 (2008).
21. X. Ji, J. Zhou, H. Guo, and S. Jiang, "3D Finite Element Simulation for the Temperature Field of Direct Metal Laser Sintering Process," J. Comput. Theoret. Nanosci. **8**, 1578-1582 (2008).
22. B. Wong, M. Menguc, and R. Vallance, "Sequential nano-patterning using electron and laser beams: A numerical methodology " J. Comput. Theoret. Nanosci. **3**, 219-230 (2006).
23. A. Poncet, "Finite-Element Simulation of Local Oxidation of Silicon," Computer-Aided Design of Integrated Circuits and Systems, IEEE Transactions on **4**, 41-53 (1985).
24. E. Rank, and U. Weinert, "A simulation system for diffusive oxidation of silicon: a two-dimensional finite element approach," Computer-Aided Design of Integrated Circuits and Systems, IEEE Transactions on **9**, 543-550 (1990).
25. C. Hollauer, H. Ceric, and S. Selberherr, "Simulation of thermal oxidation: a three-dimensional finite element approach," in *European Solid-State Device Research, 2003. ESSDERC '03. 33rd Conference on*(2003), pp. 383-386.
26. H. Y. Zheng, and Z. W. Jiang, "Femtosecond laser micromachining of silicon with an external electric field," Journal of Micromechanics and Microengineering **20**, 017001 (2010).
27. H. C. Tse, H. C. Man, and T. M. Yue, "Effect of magnetic field on plasma control during CO2 laser welding," Optics & Laser Technology **31**, 363-368 (1999).

28. H. C. Tse, H. C. Man, and T. M. Yue, "Effect of electric and magnetic fields on plasma control during CO₂ laser welding," *Optics and Lasers in Engineering* **32**, 55-63 (1999).
29. M. Gatzen, Z. Tang, and F. Vollertsen, "Effect of electromagnetic Stirring on the Element Distribution in Laser Beam Welding of Aluminium with Filler Wire " *Physics Procedia* **12**, 56-65 (2011).
30. A. Schneider, V. Avilov, A. Gumenyuk, and M. Rethmeier, "Laser Beam Welding of Aluminum Alloys Under the Influence of an Electromagnetic Field," *Physics Procedia* **41**, 4-11 (2013).
31. W. T. Silfvast, *Laser Fundamentals* (Cambridge University Press, 2008).
32. J. Hecht, "Short history of laser development," *Optical Engineering* **49**, 091002-091023 (2010).
33. D. Basting, and G. Marowsky, *Eximer Laser Technology* (Springer-Verlag Berlin Heidelberg 2005).
34. M. Csele, *Fundamentals of Light Sources and Lasers* (John Wiley & Sons, Inc. , 2004).
35. A. Einstein, "Bemerkung zu P. Jordans Abhandlung „Zur Theorie der Quantenstrahlung“, " *Z. Physik* **31**, 784-785 (1925).
36. N. B. Dahotre, and S. P. Harimkar, *Laser Fabrication and Machining of Materials* (Springer Science + Business Media, LLC., 2008).
37. R. Paschotta, *Encyclopedia of laser physics and technology* (Wiley-VCH, 2008).
38. E. Kannatey-Asibu, *Principles of laser materials processing* (Wiley, 2009).
39. M. V. Allmen, and A. Blatter, *Laser-Beam Interactions With Materilas: Physical Princilpes and Applications* (Springer, 1994).
40. N. P. Mahalik, *Micromanufacturing and Nanotechnology* (Springer, 2006).
41. W. Clark, "Micromachining Handbook " (2009), http://www.ultrafastmachining.com/mmhandbook_3.html.

42. L. Li, M. Hong, M. Schmidt, M. Zhong, A. Malshe, B. Huis in'tVeld, and V. Kovalenko, "Laser nano-manufacturing – State of the art and challenges," *CIRP Annals - Manufacturing Technology* **60**, 735-755 (2011).
43. Sandoghdar, "Beating the diffraction limit," *Physics world* **14**, 29-33 (2001).
44. D. Bäuerle, *Laser Processing and Chemistry* (Springer, 2000).
45. J. C. Miller, *Laser Ablation: Principles and Applications* (Springer, New York, 1994).
46. I. Nishidate, N. Tanaka, T. Kawase, T. Maeda, T. Yuasa, Y. Aizu, T. Yuasa, and K. Niizeki, "Visualization of peripheral vasodilative indices in human skin by use of red, green, blue images," *Journal of Biomedical Optics* **18**, 061220-061220 (2012).
47. J. Ihlemann, "Micro patterning of fused silica by laser ablation mediated by solid coating absorption," *Applied Physics A: Materials Science & Processing* **93**, 65-68 (2008).
48. J. D. Pedarnig, M. Peruzzi, H. Salhofer, R. Schwödiauer, W. Reichl, and J. Runck, "F2-laser patterning of GaPO₄ resonators for humidity sensing," *Applied Physics A: Materials Science & Processing* **80**, 1401-1404 (2005).
49. M. Peruzzi, J. D. Pedarnig, H. Sturm, N. Huber, and D. Bäuerle, "F 2 - laser ablation and micro-patterning of GaPO 4," *EPL (Europhysics Letters)* **65**, 652 (2004).
50. M. Eyett, D. Bauerle, W. Wersing, and H. Thomann, "Excimer-laser-induced etching of ceramic PbTi_{1-x}Zr_xO₃," *Journal of Applied Physics* **62**, 1511-1514 (1987).
51. J. Bekesi, J. Meinertz, J. Ihlemann, and P. Simon, "Fabrication of large-area grating structures through laser ablation," *Applied Physics A: Materials Science & Processing* **93**, 27-31 (2008).
52. J. Ihlemann, S. Müller, S. Puschmann, D. Schäfer, M. Wei, J. Li, and P. R. Herman, "Fabrication of submicron gratings in fused silica by fused silica by

- F₂-laser ablation " *Applied Physics A: Materials Science & Processing* **76**, 751-753 (2003).
53. J. Bovatsek, A. Tamhankar, R. S. Patel, N. M. Bulgakova, and J. Bonse, "Thin film removal mechanisms in ns-laser processing of photovoltaic materials," *Thin Solid Films* **518**, 2897-2904 (2010).
54. M. Green, "Polycrystalline silicon on glass for thin-film solar cells," *Applied Physics A: Materials Science & Processing* **96**, 153-159 (2009).
55. S. Haas, G. Schöpe, C. Zahren, and H. Stiebig, "Analysis of the laser ablation processes for thin-film silicon solar cells," *Applied Physics A: Materials Science & Processing* **92**, 755-759 (2008).
56. W. Guo, Z. B. Wang, L. Li, D. J. Whitehead, B. S. Luk'yanchuk, and Z. Liu, "Near-field laser parallel nanofabrication of arbitrary-shaped patterns," *Applied Physics Letters* **90**, 243101-243103 (2007).
57. K. Minoshima, A. M. Kowalewicz, I. Hartl, E. P. Ippen, and J. G. Fujimoto, "Photonic device fabrication in glass by use of nonlinear materials processing with a femtosecond laser oscillator," *Opt. Lett.* **26**, 1516-1518 (2001).
58. Y. Sikorski, A. A. Said, P. Bado, R. Maynard, C. Florea, and K. A. Winick, "Optical waveguide amplifier in Nd-doped glass written with near-IR femtosecond laser pulses," *Electronics Letters* **36**, 226-227 (2000).
59. D. C. Deshpande, A. P. Malshe, E. A. Stach, V. Radmilovic, D. Alexander, D. Doerr, and D. Hirt, "Investigation of femtosecond laser assisted nano and microscale modifications in lithium niobate," *Journal of Applied Physics* **97**, 074316-074319 (2005).
60. K. Vora, S. Kang, S. Shukla, and E. Mazur, "Fabrication of disconnected three-dimensional silver nanostructures in a polymer matrix," *Applied Physics Letters* **100**, 063120-063123 (2012).
61. Y.-L. Zhang, Q.-D. Chen, H. Xia, and H.-B. Sun, "Designable 3D nanofabrication by femtosecond laser direct writing," *Nano Today* **5**, 435-448 (2010).

62. A. Malshe, D. Deshpande, E. Stach, K. Rajurkar, and D. Alexander, "Investigation of Femtosecond Laser-Assisted Micromachining of Lithium Niobate," *CIRP Annals – Manufacturing Technology* **53**, 187-190 (2004).
63. K. Miura, J. Qiu, H. Inouye, T. Mitsuyu, and K. Hirao, "Photowritten optical waveguides in various glasses with ultrashort pulse laser," *Applied Physics Letters* **71**, 3329-3331 (1997).
64. S. Nakashima, K. Sugioka, and K. Midorikawa, "Fabrication of microchannels in single-crystal GaN by wet-chemical-assisted femtosecond-laser ablation," *Applied Surface Science* **255**, 9770-9774 (2009).
65. Y. Shimotsuma, K. Hirao, P. G. Kazansky, and J. Qiu, "Three-Dimensional Micro- and Nano-Fabrication in Transparent Materials by Femtosecond Laser," *Jpn. J. Appl. Phys.* **44**, 4735-4748 (2005).
66. K.-S. Lee, R. H. Kim, D.-Y. Yang, and S. H. Park, "Advances in 3D nano/microfabrication using two-photon initiated polymerization," *Progress in Polymer Science* **33**, 631-681 (2008).
67. K. Takada, H.-B. Sun, and S. Kawata, "Improved spatial resolution and surface roughness in photopolymerization-based laser nanowriting," *Applied Physics Letters* **86**, 071122 (2005).
68. B Tan, S. Panchatsharam, and K. Venkatakrishnan, "High repetition rate femtosecond laser forming sub-10 μm diameter interconnection vias " *J. Phys. D: Appl. Phys.* **42**, 065102 (2009).
69. K. Venkatakrishnan, P. Stanley, and L. E. N. Lim, "Femtosecond laser ablation of thin films for the fabrication of binary photomasks," *Journal of Micromechanics and Microengineering* **12**, 775 (2002).
70. K. Venkatakrishnan, B. Tan, and N. R. Sivakumar, "Sub-micron ablation of metallic thin film by femtosecond pulse laser," *Optics & Laser Technology* **34**, 575-578 (2002).
71. H. Hosono, K.-i. Kawamura, S. Matsuishi, and M. Hirano, "Holographic writing of micro-gratings and nanostructures on amorphous SiO₂ by near infrared femtosecond pulses," *Nuclear Instruments and Methods in Physics*

- Research Section B: Beam Interactions with Materials and Atoms **191**, 89-97 (2002).
72. D. Tan, Y. Li, F. Qi, H. Yang, Q. Gong, X. Dong, and X. Duan, "Reduction in feature size of two-photon polymerization using SCR500," *Applied Physics Letters* **90**, 071106-071103 (2007).
73. E. Vanagas, I. Kudryashov, S. Juodkazis, S. Matsuo, H. Misawa, and Tomasiunas, "Micrometer and Sub Micrometer-Size Structures Fabricated by Direc Writing Using Femtosecond Light Pulses," *Materials Science* **9**, 324-328 (2003).
74. Y. Shimotsuma, and K. Hirao, "Nano-Modification Inside Transparent Materials by Femtosecond Laser Single Beam," *Modern Physics Letters B* **19**, 225-238 (2005).
75. Y. Lin, M. H. Hong, W. J. Wang, Y. Z. Law, and T. C. Chong, "Sub-30 nm lithography with near-field scanning optical microscope combined with femtosecond laser," *Applied Physics A: Materials Science & Processing* **80**, 461-465 (2005).
76. A. M. Ozkan, and A. P. Maishe, "Femtosecond laser-induced periodic structure writing on diamond crystals and microclusters," *Applied Physics Letters* **75**, 3716 (1999).
77. C. B. Hogge, J. F. Schultz, D. B. Mason, and W. E. Thompson, "Physical optics of multiaperture systems," *Appl. Opt.* **27**, 5127-5134 (1988).
78. R. Volkel, H. P. Herzig, P. Nussbaum, R. Dandliker, and W. B. Hogle, "Microlens array imaging system for photolithography," *Optical Engineering* **35**, 3323-3330 (1996).
79. W. Hogle, R. Daendliker, and H. Herzig, "Lens Array Photolithography" in *US Paten*, U. Patent, ed. (US, 1992).
80. C. S. Lim, M. H. Hong, Y. Lin, Q. Xie, B. S. Luk'yanchuk, A. S. Kumar, and M. Rahman, "Microlens array fabrication by laser interference lithography for super-resolution surface nanopatterning," *Applied Physics Letters* **89**, 191125-191123 (2006).

81. Y. Lin, M. H. Hong, T. C. Chong, C. S. Lim, G. X. Chen, L. S. Tan, Z. B. Wang, and L. P. Shi, "Ultrafast-laser-induced parallel phase-change nanolithography," *Applied Physics Letters* **89**, 041108-041103 (2006).
82. L. Shi-Che, and W. Homg-Nian, "Near-field photolithography by a fiber probe," in *Nanotechnology, 2001. IEEE-NANO 2001. Proceedings of the 2001 1st IEEE Conference on*(2001), pp. 36-39.
83. S. Sun, and G. J. Leggett, "Generation of Nanostructures by Scanning Near-Field Photolithography of Self-Assembled Monolayers and Wet Chemical Etching," *Nano Letters* **2**, 1223-1227 (2002).
84. S. Sun, and G. J. Leggett, "Matching the Resolution of Electron Beam Lithography by Scanning Near-Field Photolithography," *Nano Letters* **4**, 1381-1384 (2004).
85. M. H. Hong, Y. Lin, G. X. Chen, L. S. Tan, Q. Xie, B. Lukyanchuk, L. P. Shi, and T. C. Chong, "Nano-patterning by pulsed laser irradiation in near field," *Journal of Physics: Conference Series* **59**, 64 (2007).
86. T. C. Chong, M. H. Hong, and L. P. Shi, "Laser precision engineering: from microfabrication to nanoprocessing," *Laser & Photonics Reviews* **4**, 123-143 (2010).
87. Y. Kawata, C. Egami, O. Nakanura, O. Sugihara, N. Okamoto, M. Tsuchimori, and W. O, "Non-Optically Probing Near-Field Microscopy.," *Optics Communications* **161**, 6-12 (1999).
88. Y. Lu, W. Song, Y. Zheng, B. Luk'yanchi, and "laser Writing of Sub-Wavelength Structure on Silicon (1 0 0) Surfaces with Particle Enhanced Optical Irradiation," *JETP Letters* **72**, 457-459 (2000).
89. M. Hasegawa, T. Ikawa, M. Tsuchimori, O. Watanabe, and Y. Kawata, "Topographical Nanostructure Patterning on the Surface of a Thin Film of Polyurethane Containing Azobenzene Moiety Using the Optical Near Field around Polystyrene Spheres," *Macromolecules* **34**, 7471-7476 (2001).

90. H. J. Münzer, M. Mosbacher, M. Bertsch, J. Zimmermann, P. Leiderer, and J. Boneberg, "Local field enhancement effects for nanostructuring of surfaces," *Journal of Microscopy* **202**, 129-135 (2001).
91. G. Wei, W. Zeng Bo, L. Lin, L. Zhu, L. y. Boris, and J. W. David, "Chemical-assisted laser parallel nanostructuring of silicon in optical near fields," *Nanotechnology* **19**, 455302 (2008).
92. Z. Wang, W. Guo, A. Pena, D. Whitehead, B. Luck'yanchuk, L. Li, Z. Liu, Y. Zhou, and M. Hong, "Laser Micro/Nano Fabrication in Glass with Tunable-Focus Particle Lens Array.," *Optics Express*. **16**, 19706-19711 (2008).
93. A. Pena, Z. Wang, D. Whitehead, and L. Li, "Direct writing of micro/nano-scale patterns by means of particle lens arrays scanned by a focused diode pumped Nd:YVO4 laser," *Applied Physics A: Materials Science & Processing* **101**, 287-295 (2010).
94. W. Guo, Z.-B. Wang, L. Li, Z. Liu, B. Luk'yanchuk, and D. Whitehead, "Laser Parallel Nanopatterning of Lines and Curves by Micro-Particle Lens Arrays.," *Journal of Laser Micro/Nanoengineering* **2**, 212 (2007).
95. L. Li, W. Guo, Z.-B. Wang, Z. Liu, D. Whitehead, and B. S. Luk'yanchuk, "Large Area Laser Nanotexturing with User-Defined Patterns.," *Journal of Micromechanics and Micro-engineering* **19**, 064002 (2009).
96. K. Ashfaq, W. Zengbo, A. S. Mohammad, J. W. David, and L. Lin, "Parallel near-field optical micro/nanopatterning on curved surfaces by transported micro-particle lens arrays," *Journal of Physics D: Applied Physics* **43**, 305302 (2010).
97. K. H. Leitz, U. Quentin, B. Hornung, A. Otto, I. Alexeev, and M. Schmidt, "Ultrafast Microsphere Near-field Nanostructuring," in *Frontiers in Ultrafast Optics: Biomedical, Scientific, and Industrial Applications Xi*, A. Heisterkamp, J. Neev, and S. Nolte, eds. (Spie-Int Soc Optical Engineering, Bellingham, 2011).

98. T. Miyanishi, T. Sakai, N. Nedyalkov, and M. Obara, "Femtosecond-laser nanofabrication onto silicon surface with near-field localization generated by plasmon polaritons in gold nanoparticles with oblique irradiation," *Applied Physics A: Materials Science & Processing* **96**, 843-850 (2009).
99. N. N. Nedyalkov, H. Takada, and M. Obara, "Nanostructuring of silicon surface by femtosecond laser pulse mediated with enhanced near-field of gold nanoparticles," *Applied Physics A: Materials Science & Processing* **85**, 163-168 (2006).
100. A. Ashkin, J. M. Dziedzic, J. E. Bjorkholm, and S. Chu, "Observation of a single-beam gradient force optical trap for dielectric particles," *Opt. Lett.* **11**, 288-290 (1986).
101. E. McLeod, and C. B. Arnold, "Subwavelength direct-write nanopatterning using optically trapped microspheres," *Nat Nano* **3**, 413-417 (2008).
102. J. Y. Walz, and D. C. Prieve, "Prediction and measurement of the optical trapping forces on a microscopic dielectric sphere," *Langmuir* **8**, 3073-3082 (1992).
103. Y. Tsai, R. Fardel, and C. Arnold, "Generating Sub-Micron Features On Rough Surfaces Using Optical Trap Assisted Nano Patterning," in *AIP proceedings*(2010), pp. 457-464.
104. H. M. van Driel, J. E. Sipe, and J. F. Young, "Laser-induced coherent modulation of solid and liquid surfaces," *Journal of Luminescence* **30**, 446-471 (1985).
105. M. Birnbaum, "Semiconductor Surface Damage Produced by Ruby Lasers.," *Journal of Applied Physics* **36**, 3688-3689 (1965).
106. M. Shinoda, R. R. Gattass, and E. Mazur, "Femtosecond laser-induced formation of nanometer-width grooves on synthetic single-crystal diamond surfaces," *Journal of Applied Physics* **105**, 053102-053104 (2009).

107. M. N. W. Groenendijk, and J. Meijer, "Surface Microstructures obtained by Femtosecond Laser Pulses," *CIRP Annals - Manufacturing Technology* **55**, 183-186 (2006).
108. B. Huis in't Veld, M. Groenendijk, and H. Fischer, "Initiation of Femtosecond Laser Machined Ripples in Steel Observed by Scanning Helium Ion Microscopy.," *Journal of Laser Micro/Nanoengineering* **5**, 28-34 (2010).
109. X. Guo, R. Li, Y. Hang, Z. Xu, B. Yu, Y. Dai, B. Lu, and X. Sun, "Coherent linking of periodic nano-ripples on a ZnO crystal surface induced by femtosecond laser pulses," *Applied Physics A: Materials Science & Processing* **94**, 423-426 (2009).
110. J. E. Sipe, J. F. Young, J. S. Preston, and H. M. van Driel, "Laser-induced periodic surface structure. I. Theory," *Physical Review B* **27**, 1141 (1983).
111. T. R. Anthony, and H. E. Cline, "Surface rippling induced by surface tension gradients during laser surface melting and alloying," *Journal of Applied Physics* **48**, 3888-3894 (1977).
112. M. N. Libenson, V. S. Makin, V. A. Shiryayev, and M. J. Soileau, "Surface periodic structures under the optical damage of transparent dielectrics," in *Laser-Induced Damage in Optical Materials: 1994*, H. E. Bennett, A. H. Guenther, M. R. Kozlowski, B. E. Newnam, and M. J. Soileau, eds. (Spie - Int Soc Optical Engineering, Bellingham, 1995), pp. 676-681.
113. A. V. Bulgakov, and N. M. Bulgakova, "Dynamics of laser-induced plume expansion into an ambient gas during film deposition," *Journal of Physics D: Applied Physics* **28**, 1710 (1995).
114. S. S. Harilal, C. V. Bindhu, M. S. Tillack, F. Najmabadi, and A. C. Gaeris, "Internal structure and expansion dynamics of laser ablation plumes into ambient gases," *Journal of Applied Physics* **93**, 2380 (2003).
115. A. Bogaerts, Z. Chen, R. Gijbels, and A. Vertes, "Laser ablation for analytical sampling: what can we learn from modeling?," *Spectrochimica Acta Part B: Atomic Spectroscopy* **58**, 1867-1893 (2003).

116. J. M. Vadillo, and J. J. Laserna, "Laser-induced plasma spectrometry: truly a surface analytical tool," *Spectrochimica Acta Part B: Atomic Spectroscopy* **59**, 147-161 (2004).
117. R. K. Singh, and J. Narayan, "Pulsed-laser evaporation technique for deposition of thin films: Physics and theoretical model," *Physical Review B* **41**, 8843-8859 (1990).
118. G. Radhakrishnan, and P. M. Adams, "Pulsed-laser deposition of particulate-free TiC coatings for tribological applications," *Applied Physics A: Materials Science & Processing* **69**, S33 (1999).
119. S. Amoroso, "Modeling of UV pulsed-laser ablation of metallic targets," *Applied Physics A: Materials Science & Processing* **69**, 323-332 (1999).
120. S. I. Anisimov, D. Bäuerle, and B. S. Luk'yanchuk, "Gas dynamics and film profiles in pulsed-laser deposition of materials," *Physical Review B* **48**, 12076-12081 (1993).
121. S. Amoroso, A. Sambri, and X. Wang, "Plume expansion dynamics during laser ablation of manganates in oxygen atmosphere," *Applied Surface Science* **253**, 7696-7701 (2007).
122. A. A. Voevodin, J. G. Jones, J. S. Zabinski, Z. Czigany, and L. Hultman, "Growth and structure of fullerene-like CN_x thin films produced by pulsed laser ablation of graphite in nitrogen," *Journal of Applied Physics* **92**, 4980-4988 (2002).
123. S. S. Harilal, "Expansion dynamics of laser ablated carbon plasma plume in helium ambient " *Applied Surface Science* **172**, 103-109 (2001).
124. S. M. Park, and J. Y. Moon, "Laser ablation of graphite in an oxygen jet," *The Journal of Chemical Physics* **109**, 8124-8129 (1998).
125. R. M. Mayo, J. W. Newman, A. Sharma, Y. Yamagata, and J. Narayan, "Electrostatic measurement of plasma plume characteristics in pulsed laser evaporated carbon," *Journal of Applied Physics* **86**, 2865-2871 (1999).
126. D. Kim, H. K. Park, and C. P. Grigoropoulos, "Interferometric probing of rapid vaporization at a solid-liquid interface induced by pulsed-laser

- irradiation," International Journal of Heat and Mass Transfer **44**, 3843-3853 (2001).
127. T. Masubuchi, T. Tada, E. Nomura, K. Hatanaka, H. Fukumura, and H. Masuhara, "Laser-Induced Decomposition and Ablation Dynamics Studied by Nanosecond Interferometry. 4. A Polyimide Film†," The Journal of Physical Chemistry A **106**, 2180-2186 (2002).
128. S. H. Glenzer, K. B. Fournier, C. Decker, B. A. Hammel, R. W. Lee, L. Lours, B. J. MacGowan, and A. L. Osterheld, "Accuracy of K-shell spectra modeling in high-density plasmas," Physical Review E **62**, 2728-2738 (2000).
129. D. B. Geohegan, "Fast intensified-CCD photography of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ laser ablation in vacuum and ambient oxygen," Applied Physics Letters **60**, 2732-2734 (1992).
130. S. S. Harilal, C. V. Bindhu, and H. J. Kunze, "Time evolution of colliding laser produced magnesium plasmas investigated using a pinhole camera," Journal of Applied Physics **89**, 4737-4740 (2001).
131. C. Phipps, *Laser Ablation and its Applications* (Springer 2006).
132. J. C. R. Phipps, T. P. Turner, R. F. Harrison, G. W. York, W. Z. Osborne, G. K. Anderson, X. F. Corlis, L. C. Haynes, H. S. Steele, K. C. Spicochi, and T. R. King, "Impulse coupling to targets in vacuum by KrF, HF, and CO_2 single-pulse lasers," Journal of Applied Physics **64**, 1083-1096 (1988).
133. S. WM., *Laser material processing* (Springer, Berlin, 1991).
134. Y. Arata, N. Abe, and T. Oda, "Fundamental phenomena in high power CO_2 laser welding (Report I)," Transactions of JWRI **14**, 5-11 (1985).
135. KATAYAMA Seiji, ABE Yohei, MIZUTANI Masami, and KAWAHITO Yousuke, "Deep Penetration Wedling with High-Power under Vacuum," Transactions for JWRI **40**, 15-19 (2011).
136. Ishide T et al., in *Proceeding of LAMP'87*(Osaka, 1987), p. 187.
137. Michaelis A et al., in *CO2 lasers and applications II*(Hague, 1990), p. 231.

138. A. Poueyo-Verwaerde, R. Fabbro, G. Deshors, A. M. de Frutos, and J. M. Orza, "Experimental study of laser-induced plasma in welding conditions with continuous CO₂ laser," *Journal of Applied Physics* **74**, 5773 (1993).
139. Z. Sun, A. S. Salminen, and T. J. I. Moisio, "Quality improvement of laser beam welds by plasma control," *Journal of Materials Science Letters* **12**, 1131-1133 (1993).
140. M. Gatzert, "Influence of Low-frequency Magnetic Fields During Laser Beam Welding of Aluminium with Filler Wire," *Physics Procedia* **39**, 59-66 (2012).
141. D. Bäuerle, *Laser Processing and Chemistry* (Springer, 2002).
142. E. D. Palik, ed. *Handbook of Optical Constants of Solids* (Elsevier, 1998).
143. N. T. Vladimirov, and F. H. K. Alexander, "Suppression of melt flows in laser ablation: application to clean laser processing," *Journal of Physics D: Applied Physics* **32**, 1526 (1999).
144. D. V. Hutton, *Fundamental of finite element analysis* (Mc Grow Hill, 2004).
145. H. Farrokhi, W. Zhou, H. Zheng, and Z. Li, "Numerical Simulation of Non-ablative Laser Texturing of Silicon Surface with a Continuous Wave Fiber Laser," *Journal of Computational and Theoretical Nanoscience* **11**, 1-5 (2014).
146. K. Abderrazak, W. Kriaa, W. Ben Salem, H. Mhiri, G. Lepalec, and M. Autric, "Numerical and experimental studies of molten pool formation during an interaction of a pulse laser (Nd:YAG) with a magnesium alloy," *Optics & Laser Technology* **41**, 470-480 (2009).
147. X. Wang, Y. Qin, B. Wang, L. Zhang, Z. Shen, J. Lu, and X. Ni, "Numerical and experimental study of the thermal stress of silicon induced by a millisecond laser," *Appl. Opt.* **50**, 3725-3732 (2011).
148. J. Blanc, "A revised model for the oxidation of Si by oxygen," *Appl. Phys. Lett.* **33**, 424-426 (1978).

149. V. K. Samalam, "Theoretical model for the oxidation of silicon," Appl. Phys. Lett. **47**, 736-737 (1985).
150. A. Fargeix, and G. Ghibaudo, "Role of stress on the parabolic kinetic constant for dry silicon oxidation," Journal of Applied Physics **56**, 589-591 (1984).
151. H. Z. Massoud, J. D. Plummer, and J. D. Irene, "Thermal oxidation of silicon in dry oxygen: growth-rate enhancement in the thin regime: II. physical-mechanism,," J. Electrochem. Soc **132**, 2693-2700 (1985).
152. B. E. Deal, and A. S. Grove, "General Relationship for the Thermal Oxidation of Silicon," J. Appl. Phys. **36**, 3770-3778 (1965).
153. A. Kiani, K. Venkatakrishnan, and B. Tan, "Direct patterning of silicon oxide on Si-substrate induced by femtosecond laser," Opt. Express **18**, 1872-1878 (2010).
154. James D. Plummer, Michael Deal, and P. D. Griffin, *Silicon VLSI Technology: Fundamentals, Practice, and Modeling* (Prentice Hall, 2001).
155. J. Bonse, K. W. Brzezinka, and A. J. Meixner, "Modifying single-crystalline silicon by femtosecond laser pulses: an analysis by micro Raman spectroscopy, scanning laser microscopy and atomic force microscopy," Appl. Surf. Sci. **221**, 215-230 (2004).
156. A. Y. Vorobyev, and C. Guo, "Direct observation of enhanced residual thermal energy coupling to solids in femtosecond laser ablation," Appl. Phys. Lett. **86**, 011916-011913 (2005).
157. E. M. Young, and W. A. Tiller, "Photon enhanced oxidation of silicon," Applied Physics Letters **42**, 63-65 (1983).
158. S. A. Schafer, and S. A. Lyon, "Wavelength dependence of laser-enhanced oxidation of silicon," J. Vac. Sci. Technol. **21**, 422-425 (1982).
159. B. H. Ripin, E. A. McLean, C. K. Manka, C. Pawley, J. A. Stamper, T. A. Peyser, A. N. Mostovych, J. Grun, A. B. Hassam, and J. Huba, "Large-Larmor-radius interchange instability," Physical Review Letters **59**, 2299-2302 (1987).

160. S. Okada, K. Sato, and T. Sekiguchi, "Behaviour of Laser-Produced Plasma in a Uniform Magnetic Field - Plasma Instabilities," *Jpn. J. Appl. Phys.* **20**, 157-165 (1981).
161. L. Dirnberger, P. E. Dyer, S. R. Farrar, and P. H. Key, "Observation of magnetic-field-enhanced excitation and ionization in the plume of KrF-laser-ablated magnesium," *Applied Physics A: Materials Science & Processing* **59**, 311-316 (1994).
162. D. W. Koopman, "High-beta effects and anomalous diffusion in plasmas expanding into magnetic fields," *Physics of Fluids* **19**, 670-674 (1976).
163. G. E. Jellison, and F. A. Modine, "Optical functions of silicon between 1.7 and 4.7 eV at elevated temperatures," *Physical Review B* **27**, 7466 (1983).
164. V. N. Rai, A. K. Rai, F.-Y. Yueh, and J. P. Singh, "Optical Emission from Laser-Induced Breakdown Plasma of Solid and Liquid Samples in the Presence of a Magnetic Field," *Appl. Opt.* **42**, 2085-2093 (2003).
165. S. S. Harilal, M. S. Tillack, B. O'Shay, C. V. Bindhu, and F. Najmabadi, "Confinement and dynamics of laser-produced plasma expanding across a transverse magnetic field," *Physical Review E* **69**, 026413 (2004).
166. C. Pagano, S. Hafeez, and J. G. Lunney, "Influence of transverse magnetic field on expansion and spectral emission of laser produced plasma," *Journal of Physics D: Applied Physics* **42**, 155205 (2009).
167. Y. Y. Tsui, H. Minami, D. Vick, and R. Fedosejevs, "Debris reduction for copper and diamond-like carbon thin films produced by magnetically guided pulsed laser deposition," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **20**, 744-747 (2002).
168. R. Jordan, D. Cole, and J. G. Lunney, "Pulsed laser deposition of particulate-free thin films using a curved magnetic filter," *Applied Surface Science* **109-110**, 403-407 (1997).
169. Y. Y. Tsui, D. Vick, and R. Fedosejevs, "Guiding and confinement of a laser produced plasma by a curved magnetic field," *Applied Physics Letters* **70**, 1953-1955 (1997).

170. C. de Julián Fernández, J. L. Vassent, and D. Givord, "Thin film deposition by magnetic field-assisted pulsed laser assembly," *Applied Surface Science* **138-139**, 150-154 (1999).
171. E. J. Button, and A. H. Guenther, "Effect of high magnetic fields on the threshold of laser-induced gas breakdown," *Journal of Applied Physics* **47**, 522-530 (1976).
172. T. J. M. Boyd, and J. J. Sanderson, *The Physics of Plasmas* (Cambridge University Press Cambridge, U.K., New York, 2003).
173. S. Harilal, M. Tillack, B. O'Shay, C. Bindhu, and F. Najmabadi, "Confinement and dynamics of laser-produced plasma expanding across a transverse magnetic field," *Physical Review E* **69** (2004).
174. X. Zeng, X. L. Mao, R. Greif, and R. E. Russo, "Experimental investigation of ablation efficiency and plasma expansion during femtosecond and nanosecond laser ablation of silicon," *Applied Physics A: Materials Science & Processing* **80**, 237-241 (2005).
175. D. R. Cohn, G. J. Raff, R. L. Brooks, N. G. Loter, and W. Halverson, "Beam self-focussing in a laser-produced plasma in a magnetic field," *Physics Letters A* **49**, 95-96 (1974).
176. W. M. Steen, "Arc augmented laser processing of materials," *Journal of Applied Physics* **51**, 5636-5641 (1980).
177. G. Campana, A. Fortunato, A. Ascari, G. Tani, and L. Tomesani, "The influence of arc transfer mode in hybrid laser-mig welding," *Journal of Materials Processing Technology* **191**, 111-113 (2007).
178. B. Hu, and I. M. Richardson, "Microstructure and mechanical properties of AA7075(T6) hybrid laser/GMA welds," *Materials Science and Engineering: A* **459**, 94-100 (2007).