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Laser micromachining of biodegradable polymers and ceramics

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Laser micromachining of biodegradable polymers and ceramics

by

Vijay V. Kancharla

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Industrial Engineering

Program of Study Committee:
Shaochen Chen, Major Professor
Ranga Narayanaswami
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Iowa State University

Ames, Iowa

2002

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Graduate College
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This is to certify that the Master's thesis of
Vijay V. Kancharla
has met the thesis requirements of Iowa State University

Signatures have been redacted for privacy

Dedicated to my Parents and Grandparents

TABLE OF CONTENTS

LIST OF FIGURES	vi
LIST OF TABLES	viii
NOMENCLATURE	ix
ACKNOWLEDGEMENTS	xi
ABSTRACT	xii
CHAPTER 1. INTRODUCTION	1
Properties of laser light	1
Types of lasers	2
Lasers for micromachining	7
Research Objectives	9
Thesis Organization	10
CHAPTER 2. LASER MICROMACHINING OF BIODEGRADABLE POLYMERS	11
Introduction	11
Theoretical Background	16
Experimental Setup	18
Results and Discussion	21
Summary	31
CHAPTER 3. LASER MICROMACHINING OF CERAMICS	33
Introduction	33
Theoretical Background	36

Materials and Procedures	38
Results and Discussion	41
Summary	44
CHAPTER 4. CONCLUSIONS	45
Conclusions for present work	45
Recommendations for future work	46
APPENDIX A. Scanning Electron Microscope	48
APPENDIX B. Surface Profilometer	50
REFERENCES	51

LIST OF FIGURES

Figure 1.1	UV range in the electromagnetic spectrum	3
Figure 1.2	Nd: YAG energy level system	6
Figure 2.1	Chemical structure of PCL	14
Figure 2.2	Chemical structure of Polystyrene	14
Figure 2.3	Laser micromachining setup for biodegradable polymers	20
Figure 2.4	Etching depth Vs $\ln(F/F_{th})$ for holes at 266-nm wavelength SEM image of hole drilled in PVA (entry)	22
Figure 2.5	SEM image of 5.36 μm hole (at exit) drilled at 0.735 mJ	23
Figure 2.6	266-nm Nd: YAG (left) and 193-nm excimer (right) laser etched holes in PVA	24
Figure 2.7	Laser energy Vs hole size	25
Figure 2.8	SEM images of an array of holes (at the exit)(top) and image of holes at the entry (bottom)	25
Figure 2.9	Etching Depths Vs $\ln(F/F_{th})$ for channels at 308-nm Wavelength	26
Figure 2.10	SEM image of Microchannels etched at 17 mJ (top) and 22 mJ (bottom)	27
Figure 2.11	Microchannel etched on PVA at 308-nm wavelength.	27
Figure 2.12	Channel etched on PVA at 308-nm wavelength (left) and at 193-nm (right)	29

Figure 2.13	Comparison of laser cut quality for PDLA at 308-nm (Left) and 193 nm (right)	30
Figure 2.14	Excimer laser cuts in PS at 193-nm (left) and 308-nm (right)	30
Figure 2.15	Excimer laser cuts in PCL at 193-nm	31
Figure 3.1	Relation between wavelength and absorption properties for ceramics	35
Figure 3.2	Holes etched at 18 mJ for a) 1000 b) 1400 pulses and c) 2000 pulses	42
Figure 3.3	Array of 193-nm excimer etched holes	43
Figure 3.4	Microchannel etched at 193-nm laser wavelength	43
Figure 3.5	Array of channels etched at 193-nm laser wavelength	44

LIST OF TABLES

Table 1.1	Partial listing of excimer laser types	5
Table 2.1	Polymer bond dissociation energies	18
Table 2.2	Properties of lasers used in the experiments	19
Table 3.1	Properties of Al ₂ O ₃ ceramics	39

NOMENCLATURE

c	velocity of light, 3×10^8 m/sec
f_q	frequency, Hz
E	energy of photons, eV
h	Planck's constant, 6.634×10^{-34} Js
d_s	spot size, μm
f	focal length, inches
D	diameter of laser beam, mm
F_{th}	Thershold fluence, J/Cm^2
F	fluence, J/Cm^2
L_f	etching depth, μm

Greek letters

λ	Wavelength, μm
α	absorption co-efficient, cm^{-1}

Acronyms

CW	continuous wave
HAZ	heat affected zone
Nd: YAG	Neodymium doped Yttrium Aluminum Garnet
He-Ne	helium-neon

IR	infrared
UV	ultra-violet
SEM	scanning electron microscope
MEMS	micro electro mechanical systems
CVL	copper vapour lasers
Ar	argon
Kr	krypton
Xe-Cl	xenon-chloride

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ABSTRACT

As feature sizes fall below one thousandth of an inch, mechanical approaches to drilling, patterning, cutting and shaping of materials must be replaced with photon or particle beam techniques, and lasers play an important role. Lasers are the most promising tools for micromachining because the beam is highly localized, i.e. it can be focused down to the size of the wavelength (in the order of microns and smaller). The beam properties of laser make it the perfect tool for micromachining applications. The objective of this work is to pattern microholes and microchannels on polymers and ceramics and to study the ablation characteristics under laser irradiation.

Biodegradable polymers, PVA, PDLA, PCL and PS have been micromachined by UV lasers for applications in biomedical engineering. Frequency quadrupled Nd: YAG laser at a wavelength of 266-nm was used to drill microholes on the polymer. A microfilter is fabricated by drilling an array of microholes on the polymer, which finds applications for bioseparations. The smallest size of the hole obtained was 5 μm in diameter. 3-D microchannels are etched on the polymers by 308-nm Xe-Cl and 193-nm excimer lasers for applications in artificial nerve regeneration. The channels patterned were 33 to 65 μm wide and 22 to 123 μm deep. This work on biodegradable polymers is first of its kind.

Ceramics are one of the important Micro Electro Mechanical Systems (MEMS) packaging materials currently used to fabricate many microdevices. In this

work micromachining of hard-to-machine material, ceramics is performed with Xe-Cl excimer lasers at 308-nm and 193-nm wavelengths. Microholes and microchannels are machined on the Al_2O_3 ceramics. Microholes are widely used in microelectronic circuits and acts as interconnects between multilayer modules and the channels are used in ceramic microfluidic devices. The experimental results and morphology of the materials after laser ablation are reported.

CHAPTER 1

INTRODUCTION

Properties of laser light

The light emitted by a laser is an electromagnetic radiation consisting of vibrating electric and magnetic fields. In all portions of the optical spectrum, electromagnetic radiation has the same velocity (velocity of light) and same electromagnetic nature, but has different frequencies. The relation between the frequency and wavelength (length over which the wave repeats itself) is valid for all types of electromagnetic radiation is given by the equation below (λ =Wavelength, f_q = Frequency, c = Velocity of light).

$$\lambda f_q = c \quad (1.1)$$

The electromagnetic radiation is also described as particle-like character. In some cases light acts as discrete particle amounts or quanta of energy called photons carrying a discrete amount of energy.

The properties of the laser light, which make it unique from the conventional light sources, are 1) directivity, 2) brightness, 3) coherence and 4) monochromaticity. The laser beams are highly directional, which implies very small divergence. The directionality of the laser beam is described in terms of full angle beam divergence, which is twice the angle that the outer edge of the beam makes with the center of the beam. This beam divergence is unavoidable because of diffraction of light. The brightness of a light source is defined as the power emitted per unit surface area per unit solid angle. The two types of coherence in electromagnetic radiation are spatial

coherence and temporal coherence and laser light is highly coherent. Monochromaticity refers to the pure wavelength of light with very narrow laser linewidths.

Types of lasers

Lasers are classified according to the type of lasing medium used. The three lasing mediums used are solid state medium, gaseous medium, and liquid medium. Some examples of solid state lasers are ruby laser and Nd: YAG lasers. CO₂, He-Ne, and excimer lasers are the most popular gas lasers used in the industry. Dye lasers are examples of liquid medium lasers.

Lasers are also classified according to the region they fall in the electromagnetic spectrum. The electromagnetic spectrum ranges from radio waves to Gamma rays. The wavelengths in which the laser light falls in the spectrum is between Infrared and the ultraviolet region. Lasers in this region are classified into three types. They are infrared lasers, visible lasers, and ultraviolet lasers. Some examples of infrared (IR) lasers are the CO₂ and Nd: YAG lasers. He-Ne lasers emit red laser light and fall in the visible laser category. Excimer and frequency quadrupled Nd: YAG lasers fall in the ultraviolet (UV) spectrum. The basics of UV lasers and the working principle of these lasers are discussed in detail below.

The "ultraviolet" is a small portion of the electromagnetic spectrum. UV light is roughly defined from 100-nm to 400-nm wavelength regions of the electromagnetic spectrum. The UV range of the light is between longer wavelength visible light (400-nm to 700-nm) and shorter wavelength X-ray (10-nm to 100-nm). The UV region can

be divided into four sub-regions as 1) Far UV (100-nm to 200-nm), 2) Deep UV (180-nm to 280-nm), 3) Mid UV (280-nm to 315-nm), and 3) Near UV (315-nm to 400-nm). Lasers with the wavelength in this portion of the electromagnetic spectrum are called UV lasers (Hecht.J, 1988).

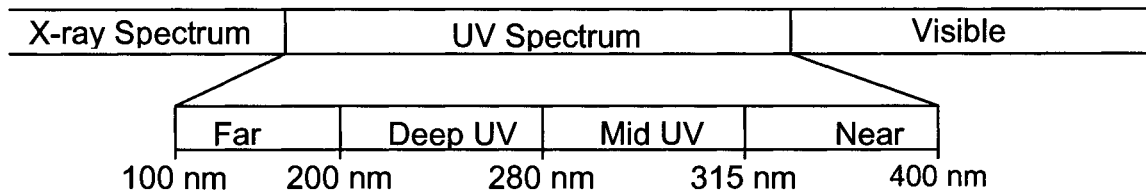


Figure 1.1 UV range in the electromagnetic spectrum

There are different kinds of UV laser. Some of the popular and commercial UV lasers are Excimer lasers, argon ion lasers, frequency tripled and quadrupled Nd: YAG lasers, fluorine lasers, helium cadmium lasers, metal vapor lasers, and nitrogen lasers. Ultraviolet wavelength exhibits unique beam properties such as high photon energy, which is very useful in a wide variety of applications. Typical applications fall into three broad categories: 1) industrial, 2) scientific, and 3) medical.

Industrial applications include photolithography, micromachining of materials such as polymers, ceramics, glass etc., and fiber Bragg gratings in optical fibers, inspection, and testing and manufacture of masks. Scientific applications of UV laser are spectroscopy, materials research, Dye laser pumping and applied research. The major medical applications are in laser vision corrections and in cardiovascular surgery.

The excimer laser is a family of pulsed lasers operating in the ultraviolet region of the electromagnetic spectrum. The name excimer is derived from the words "excited dimer" which means that the active medium consists of gaseous atoms that are bound only in the excited state to form molecules (David. J, 1995). The source of emission is a fast electrical discharge in a high pressure mixture of rare gas such as argon, krypton and xenon. The bulk of the gas mixture is a buffer gas usually helium or neon which mediates the transfer and does not act as a light emitting species.

Noble gases (Ar, Kr or Xe etc.) cannot form compounds with other elements under normal conditions. When these noble gases are excited in the laser cavity with electrical discharge method or electron beam method or the combination of the two, noble gas atoms can be ionized. The ionized atoms attract neutral atoms (such as fluorine F_2 or chlorine Cl_2) to form ionized molecules, these molecules are known as excimer complexes (exciplex). This bond is very strong but lasts only a few nanoseconds. These components can exist only temporally when the noble gas is in the excited electronic state and when the noble gas atoms are no longer in the excited state, the compound molecule dissociates into their elemental components. This process is accompanied by the release of binding energy and this released binding energy is in the form of photon energy. The stronger the binding energy, the shorter the wavelength. Typical excimer complexes include krypton fluoride (KrF), xenon fluoride (XeF), argon fluoride (ArF) and xenon chloride (XeCl). The particular combination of a rare gas and the halogen determines the output wavelength of the

excimer laser. Some of the excimer lasers commonly used is listed in Table 1.1 (Chang., 1994).

Since the wavelengths of excimer laser are in the UV region of the spectrum, the wavelengths are small and have high photon energies. This feature makes the excimer laser a very good choice for many materials processing applications and find many applications in medical, research, and telecommunication industry.

Table 1.1 Partial listing of excimer laser types

Lasing Molecule	Wavelength (nm)	Photon energy (eV)	Average Power (Watt)
F ₂	157	7.9	< 5
ArF	193	6.4	~30
KrCl	222	5.6	~30
KrF	248	5.0	50-100
XeCl	308	4.0	50-150
XeF	351	3.5	< 50

The Nd: YAG laser is an optically pumped solid-state laser that can produce very high-power emissions. The fundamental wavelength of the Nd: YAG laser is 1064-nm, in the IR region of the spectrum. The lasing medium is the colorless, isotropic crystal Y₂Al₅O₁₂ (Yttrium-Aluminum Garnet - YAG). When used in a laser, about 1% of the Yttrium is replaced by Neodymium. The energy levels of the Nd³⁺

ion are responsible for the fluorescent properties, which are the active particles in the amplification process.

The Nd: YAG crystals are excited by absorbing light from a krypton flash lamp. The crystal absorbs energy in two 730-760 nm and 790-820 nm pumping bands. The lamp provides light in both the bands and causes the molecules in the crystal to excite to the E_4 pump band. The molecules radiate heat in the $E_4 - E_3$ transition and the $E_2 - E_1$ transition. The four level energy system of the Nd: YAG laser is shown in figure 1.2 (David et al., 1995).

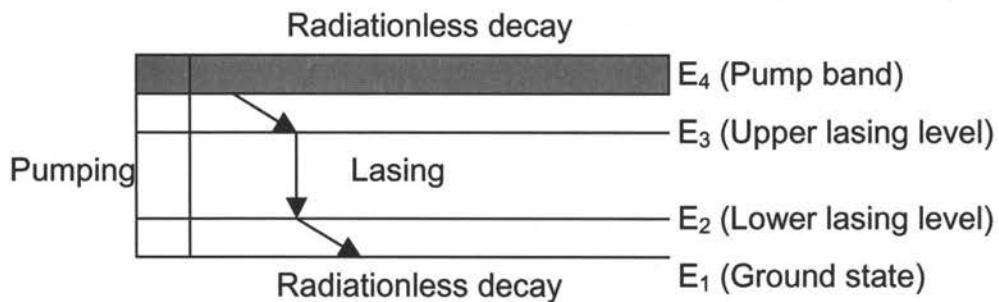


Figure 1.2 Nd: YAG energy level system

Optical crystals are used in the harmonic generator to produce frequency-multiplied wavelengths of the fundamental wavelength. KD*P crystals are good harmonic generators because of their high nonlinearity, excellent UV transmission and high damage resistance. The fundamental wavelength (1064-nm) is sent through the harmonic generator to produce both visible and UV laser beams (Lizotte., 1994). The second harmonic generator (doubled) produces 532-nm wavelength, the third harmonic generator (tripled) produces 335-nm wavelength and the fourth (quadrupled) produces the 266-nm wavelength. The Nd: YAG laser is

used for many industrial applications such as medical, aerospace, automotive, manufacturing etc and in many research and scientific uses.

Lasers for micromachining

Laser Micromachining is a combination of laser-assisted technological processes for precise treatment, modification and synthesis of materials in the micrometer domain. It is a general term that covers common processes such as drilling, patterning and marking in the order of microns that affect the physical properties of the material. Almost any kind of material can be processed with lasers because of their unique beam properties. Materials such as metals, ceramics, dielectrics, polymers, diamonds etc have been micromachined successfully (James, et al 1998, Kruger, et al 1996).

Lasers can generate very short pulses of light of a single wavelength, a characteristic that allows for the deposition of a great amount of energy onto a selected region of material. Among the many types of lasers now in use (CO₂, Nd:YAG, excimer, dye, argon-ion, diode, etc.), each has its own unique properties and capabilities suited to particular applications. Factors that determine the type of laser to use for a particular application include laser wavelength, energy, power, and temporal and spatial modes; material type; feature sizes and tolerances; processing speed; and cost. Laser beam properties and the material properties are the important factors to be considered when modeling the laser material interactions. The main laser beam parameters that effect micromachining processes are: beam energy, spot size, power density, transverse mode, wavelength, pulse shape and

duration, and polarization. Material properties such as surface reflectivity, specific heat, and thermal diffusivity affects the machining process as well.

The wavelength of the beam is an important parameter for micromachining. It is known that the electromagnetic radiation carries a discrete amount of energy in photons. The energy of the photons is given by the equation below (h = Planck's constant).

$$E = hf = hc/\lambda \quad (1.2)$$

It can be seen that as the wavelength of light decreases the energy of photon increases. High photon energies are available in the UV spectrum and it offers non-thermal machining of organic materials. The laser beam's wavelength also places a theoretical limit on how small the laser beam can be focussed.

Short pulse widths play an important role in micromachining. Short pulse width lasers such as femtosecond lasers deposit the energy into the material in time scales smaller than the transfer time of energy to the bulk of material, resulting in higher ablation and negligible thermal stresses.

Spot size of the beam affects the size of features. The smaller the spot size, the smaller would be the features. The area of the spot size can be calculated as (D= diameter of laser beam)

$$d_s = 4\lambda f/\pi D \quad (1.3)$$

UV and visible laser with nanosecond pulse duration and high pulse repetition rates have demonstrated the ability to machine a wide variety of materials with sub-micron precision and less heat affected zones (HAZ). Manufacturing applications include fuel injection components, inkjet printers and microdrilling of micromoulds,

via hole drilling in printed circuit boards, and silicon machining (Metev and Veiko, V, 1998)

Research Objectives

Micromachining is gaining more and more importance these days, demanding new micro fabrication tools. It is often desirable to build microstructures or etch microfeatures in many materials. As the feature size falls into the micron range, conventional mechanical approaches to cutting, drilling and processing materials like metal, ceramic, glass, diamonds or polymers must be replaced by new techniques and lasers are a good choice.

In this work micromachining of biodegradable polymers and micro electro mechanical systems (MEMS) packaging materials such as ceramics and polymers has been investigated with UV lasers.

The objectives of this research work are:

1. To conduct experimental investigations on biodegradable polymers such as Poly-Vinyl-Alcohol (PVA), Poly-D-Lactic-Acid (PDLA), Poly (epsilon) Caprolactone (PCL) and polymer Polystyrene (PS) by UV laser ablation for applications in biomedical engineering.
2. To study the effect of laser wavelength on the quality of machined features in the polymers.
3. To model the laser ablation mechanisms of the polymers.
4. To conduct preliminary investigation on processing MEMS packaging materials such as ceramics.

Thesis Organization

This work aims at investigating the process parameters, laser material interactions, and feasibility of micromachining biodegradable polymers and ceramics by UV lasers. Excimer lasers and frequency multiplied Nd: YAG laser was used to study the ablation process.

Chapter 2 deals with micromachining of biodegradable polymeric materials PVA, PDLA, PCL and polymer PS. These are important polymers used for potential applications in artificial nerve regeneration of biomedical research. Microchannels were etched by an excimer laser at 193-nm and 308-nm wavelengths and microholes were drilled by a frequency multiplied YAG laser on both these materials. The ablation rates and the effect of fluence on the structures was studied and plotted.

Chapter 3 presents UV laser micromachining of hard-to-machine material, ceramics. Microholes were drilled on the ceramic substrates for applications in interconnects and microelectronics industry. Micro channels etched find applications in ceramic-based micro-fluidic devices.

Chapter 4 summarizes the results and discussions of the current study and suggest directions for future research work in processing these materials on the nano- and micro- scale.

CHAPTER 2

LASER MICROMACHINING OF BIODEGRADABLE POLYMERS

In this chapter UV laser micromachining of biodegradable polymers is presented that find applications in biomedical engineering. Parametric studies have been conducted on biodegradable polymers, Poly-vinyl Alcohol (PVA) and Poly-D-Lactic Acid (PDLA), Poly (epsilon-caprolactone) (PCL) and polymer Polystyrene (PS) to produce microchannels and microholes. Laser patterning of microchannels is studied using a 308-nm Xe-Cl excimer laser and 193-ArF excimer laser. Laser microdrilling is studied using a frequency quadrupled Q-switched Nd: YAG laser at 266-nm wavelength.

Introduction

In the field of biomedical engineering, micro devices such as implantable drug delivery systems are currently being developed. At present the substrate materials used for fabricating most of the micro devices are silicon or glass using integrated circuit (IC) techniques (Lin et al., 1999). A major disadvantage of any nonbiodegradable device is that it must be removed surgically once the drug is exhausted (Sudesh, K. G., 1986). It is advantageous to design and fabricate such micro devices using biodegradable polymers because they would naturally degrade and disappear in the tissue over a period of time. Biodegradable systems on the other hand, should be thoroughly checked from the toxicological point of view with regard to their effect on tissue and the mode of metabolism. Currently some of the

biodegradable drug delivery systems find applications in fertility control, treatment of narcotic addicts, and antimalarials (Schwope et al., 1977).

Conventional techniques cannot deliver cost-effective solutions to produce micro-patterns on the polymer surface. Electron beam etching produces too much heat and degrade the polymer very fast (Matsui et al., 1995). Photolithography involves multiple steps in the process. Techniques such as atomic force microscopy (AFM) that utilizes mechanical forces to etch the surface are very slow and cannot be used reliably and conveniently to etch large surface areas (Gannepalli et al., 1998). Therefore, there is an acute need for new state-of-the-art techniques that avoid problems associated with the current techniques. Researchers in the biochemical field have developed some non-photolithography techniques such as soft lithography techniques for polymer microfabrication. Soft lithography techniques include microcontact printing, micromolding in capillaries, microtransfer molding, replica molding, imprinting, and injection molding (Qin et al., 1998). However, the utility of these techniques is often limited by the availability of appropriate masters.

Another emerging microfabrication technique for patterning the polymers is laser micromachining. Since the development of the laser technology in 1960, it has been widely used as an efficient and environment-conscious technique in industrial material processing, medicine, printing, data storage, communication, and defense (Slusher., 1999). The laser beam is focused down to several microns onto a material surface through a focusing lens. By controlling the laser parameters like beam energy, the material can be processed through scanning without damage, or melting to reshaping the surface, or ablation to machine the material in an extremely small

area. Laser micromachining offers tremendous advantages over conventional manufacturing technologies such as non-contact clean process, single-step processing, high precision and repeatability, flexible feature size and shape, no requirement of expensive vacuum equipment, and the ability to remove material selectively.

Laser micromachining has been conducted on various materials such as metals, semiconductors, ceramics, and some polymers for numerous applications in engineering (Gower., 1999). Micromachining of polymers is an important field that has both immediate and future applications in diverse fields such as medicine, MEMS, and photonics. There is a growing interest in the precise fabrication of microstructures in the field of biomedical engineering such as drug delivery systems, implants, and catheters. Much work has been conducted on various kinds of polymers (Chang et al., 1999, Wesner et al., 1999, Schmidt et al., 1998) such as Polymethylmethacrylate (PMMA), Polypropylene (PP), Polyamide (PI), etc. However, no work has been reported on processing of biodegradable polymers on the micro scale, regardless of the increasing demands of biodegradable micro devices for applications in biomedical engineering.

PVA is one of the important polymers used in biomedical engineering. The chemical structure of PVA is $[-\text{CH}_2-\text{CHOH}-]$. It is a water-soluble polymer and has excellent physical properties. It is used in wide range of applications such as adhesives, fibers, textile, paper sizing, and water-soluble packaging (Nagy, 1995). PDLA is a biodegradable polymer with extensive medical applications due to its

biodegradable property and is proven harmless to human body cells. PDLA has been used as a substrate material and it acts as a bridge to guide the damaged nerves to grow back together. PVA is used as the protective layer for PDLA.

Poly (ϵ -caprolactone)(PCL), an aliphatic polyesters are currently the most important biodegradable polymers in medicine. The ring-opening polymerization of ϵ -caprolactone yields a semi crystalline polymer with a melting point of 59—64°C and a glass-transition temperature of -60°C . Some of the applications of PCL are sutures and other biocompatible medical devices.

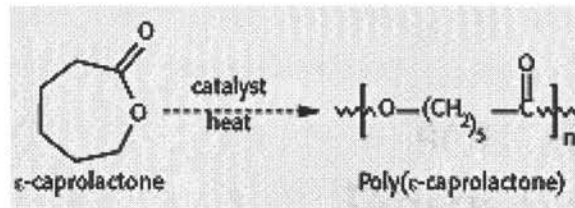


Figure 2.1 Chemical structure of PCL.

Polystyrene (PS) homopolymer, known as "crystal" polystyrene in the trade, is an amorphous, transparent and colorless commodity thermoplastic that is rigid, relatively hard and brittle. It has good electrical properties, excellent gamma radiation resistance and can be radiation sterilized but has poor chemical and UV resistance. Polystyrene is widely used as structural foam and expanded into beads



Figure 2.2 Chemical structure of Polystyrene

for packaging and cushioning. This polymer has a melting point of 270C and glass transition temperature of 100C.

The wavelength of the laser is an important parameter considered for machining polymers. When fabricating devices for applications in biomedical engineering, care should be taken to minimize the thermal damage to the device. Micromachining with nanosecond green or infrared lasers have strong thermal effects (Chen et al., 2000), whereas the UV wavelength range offers higher photon energy to break the material chemical bonds directly without significant heat transfer to the surrounding material. This important feature makes UV laser micromachining very attractive for biodegradable polymer materials since thermal damage to the non-machined part can be minimized.

The work reported here investigates the micromachining of a biodegradable polymer by UV laser irradiation. XeCl-excimer laser (308-nm) and a frequency quadrupled Nd: YAG laser (266-nm) are used to produce micro channels and micro holes on a PVA and PDLA substrates respectively. Micro channels find applications in nerve regeneration of biomedical research. The nerve cells have the ability to recognize three-dimensional structures and these 3-D micro channels act as a bridge to guide the damaged nerves to grow back together. An array of micro holes is drilled on the polymer, which is used as a biodegradable filter for bimolecular separation. This work on UV laser micromachining of a biodegradable polymer for applications in biomedical engineering is the first of its kind.

Theoretical Background

There has been much uncertainty and debate over the fundamental ablation mechanisms in polymers. Several photochemical and photothermal models have been developed to explain the ablation mechanisms (Jellinek et al., 1994, Arnold et al., 1999). In photochemical mechanism the photon energy of the light is used to break the chemical bonds of the polymer directly where as in photo thermal mechanism the material is ablated by melting and vaporizing the material (Chen et al, 1995). It was first reported (Kawamura et al., 1982) that when pulsed UV laser radiation falls on the surface of an organic polymer, the material at the surface is etched away in the order of microns.

The two fundamental mechanisms involved in the ablation are believed to be photochemical and photothermal mechanism. Many polymers have been etched by UV laser wavelengths for applications in microelectronics, opto-electronics and work on biopolymers led to advancements in laser surgery (Srinivisan et al., 1986). The empirical aspects of polymer etching are becoming better understood, but a complete quantitative physical and chemical description of ablative removal mechanisms is yet to be developed.

It is found that the material removal by laser ablation approximately obeys the Beer Lambert's law at lower laser fluence (Srinivasan et al., 1982). The relation between the etching depth and intensity of the laser is given by,

$$L_f = (1 / \alpha) \ln (F / F_{th}). \quad (2.1)$$

For photochemical ablation to occur, energy of the photons at that wavelength should overcome the intermolecular bond energies of the polymer. The relation between the photon energy of light and laser wavelength is given by,

$$E = 1.245 / \lambda. \quad (2.2)$$

The photon energy of the light depends on the wavelength of the light and as the wavelength increases the photon energy decreases. An UV laser with a wavelength of 266 nm has photon energy of 4.66 eV. It can be seen that for photochemical ablation to occur in polymers the photon energy of the light should be greater than the bond energy of the material. A summary of bond dissociation energies for several different types of bonds (Duley, 1996) is given in Table 2.1.

A photochemical model (Srinivasan et al., 1984) was presented, which is based on a volume change of the material after the photolysis, induced by the UV radiation. A thermal model (Luk'yanchuk et al., 1994) was presented where in a model was developed that a very high temperature was predicted for small etch depth per pulse ablation rates. A photochemical-thermal model (Srinivasan et al, 1990) was developed in which a thermal contribution to etching is added to the photochemical contribution derived from low fluence measurements. Several other theories to explain the ablation mechanism have surfaced considering issues such as absorption of light in three state chromophores (Cain., 1993). Furzikov et al. (1990) proposed a theory of the ablation mechanisms considering issues such as refractive index of polymer, microroughness, random polarization and weak focussing of the beam. Other theoretical models include dynamic model, receding

surface treatment, chromophore bleaching, plume screening, and Arrhenius type thermal activation (Sauerbrey et al., 1989, Cain et al., 1992, Brannon et al., 1991).

Table 2.1 Polymer bond dissociation energies.

Bond	Energy (eV)
H ₂	4.48
O ₂	5.12
N ₂	9.76
CO	11.09
C-C	3.62
C=C	6.40
C≡C	8.44
C-H	4.30
C-N	3.04
C=N	6.40
C≡N	9.27
C=S	4.96

Experimental Set Up

All the experiments in this work were performed in ambient air. Some of the specifications of the excimer and Nd: YAG laser used in this study is illustrated in Table 2.2. An excimer laser was used for the microchannels while a frequency quadrupled Nd: YAG laser was used for drilling microholes in the polymer.

Figure 2.3 illustrates the experimental setup of the excimer and the Nd: YAG lasers used for micromachining of the biodegradable polymers PVA and PDLA. The same set up is used for machining both channels and the holes on the biodegradable polymers.

Table 2.2 Properties of lasers used in the experiments

Properties of the excimer laser used		
Medium	XeCl	ArF
Wavelength	308 nm	193 nm
Pulse energy	150 mJ	3mJ
Repetition rate	0.1 – 30 Hz	10-100 Hz
Pulse width	10 ns	
Properties of the Nd: YAG laser used		
Medium	Nd: YAG crystal	
Wavelength	266 nm	
Pulse energy	35 mJ	
Repetition rate	1 – 10 Hz	
Pulse width	6-7 ns	

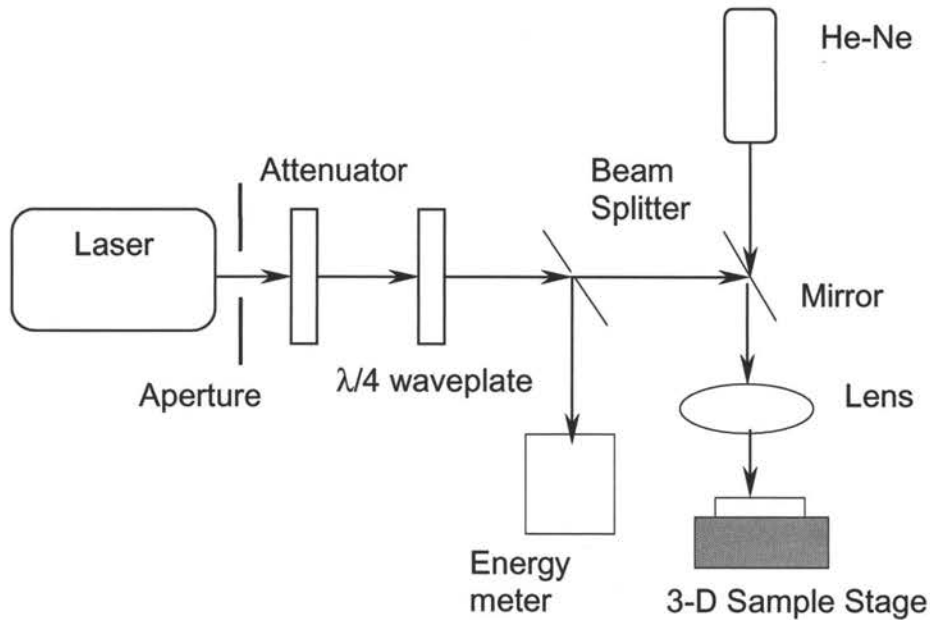


Figure 2.3 Laser micromachining setup for biodegradable polymers

A rectangular beam aperture shapes the excimer laser beam for producing the micro channels. The beam is then split into two using a 90/10 beam splitter, 10% of the beam is directed to power meter for measuring the energy and the 90% of the beam is directed to the polymer for machining. A cylindrical lens of 2-inch focal length is used to focus the laser beam onto the polymer. The polymer is mounted on a 3-D stage of a micrometer resolution. Multiple pulses were needed to ablate the polymer and a repetition rate of 1 Hz is maintained throughout the experiment. A similar setup was used for drilling holes on the polymer sample using a Nd: YAG laser. A circular aperture is used to shape the beam and a spherical lens of 1-inch focal length is used to focus the beam.

The thickness of PVA samples ranged from 90 μm to 170 μm thick. Irradiation was done with excimer laser for channels and with Nd: YAG laser for holes. In laser ablation the experimental parameters that determine the features are the laser intensity, laser wavelength and number of pulses.

The threshold energy, minimum energy required to ablate the polymer is found out. Multiple pulses above the threshold fluence were used to target the sample for ablation to occur. The etching depths per pulse were calculated by dividing the total etch depth by total number of pulses targeted. The size of micro channels is measured using a surface profilometer (for more details see Appendix B). An optical microscope and a scanning electron microscope (SEM) (for more details see Appendix A) are used to study the characteristic features of the micro holes, micro channels and the changes in the surrounding material.

Results and Discussion

In laser ablation the experimental parameters that determine the feature size are the laser intensity, laser wavelength and number of pulses. Because of the short wavelengths occurring in the UV spectrum and absorption properties of polymers, UV laser ablation of polymers is characterized as following:

1. Localized spatial interaction
2. Minimum Heat Affected zone
3. Saturation phenomena
4. Strong absorption effect
5. Threshold fluence

Microholes:

Threshold intensity for drilling holes on the polymer was found to be 0.2 mJ at 266-nm Nd: YAG laser wavelength. The experimental etch data of PVA ablated in air is shown in Figure 2.4 and the absorption coefficient (α) is obtained from the slope of the curve. At 266 nm wavelength, the absorption coefficient (α) was found out to be $0.834 \times 10^4 \text{ cm}^{-1}$. The nearly straight line in the figure agrees with the relationships that etch depth per pulse is directly proportional to the $\ln(F / F_{th})$.

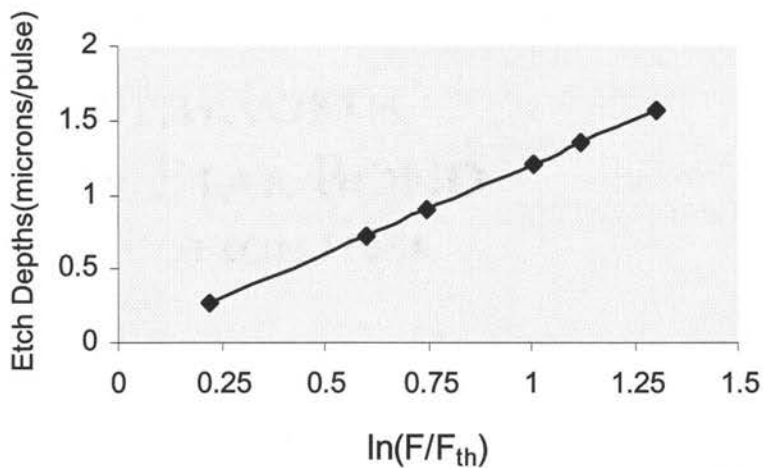


Figure 2.4 Etching depth Vs $\ln(F/F_{th})$ for holes at 266-nm wavelength

Figure 2.5 shows the morphology of the PVA polymer ablated at energy of 0.735 mJ, which is much higher than the threshold energy mentioned above. The figure shows the hole at the exit of the sample. The hole measured $5.36 \mu\text{m}$ at the exit diameter. Circularity can be improved by shaping the laser beam.

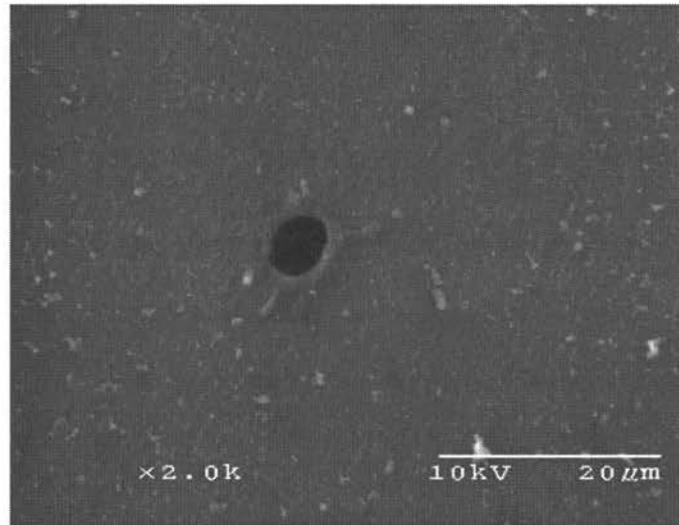


Figure 2.5 SEM image of $5.36\ \mu m$ hole (at exit) drilled at $0.735\ mJ$.

It is observed that the holes on the entry of the sample were larger than those at the exit. Fine adjustments to the hole size were able to make by regulating the exact number of pulses delivered to the target. The taper of the hole along the thickness of the sample is around 6.5 degrees. It is observed that the polymer is ablated layer by layer upon multi-pulse irradiation. The photothermal ablation mechanism is evident from the Figure 2.5, because it is seen that the molten material is ejected out of the hole and found to redeposit around the holes. This could be avoided by using lower energy fluence and lower wavelength to machine the polymers to utilize the potential of photochemical mechanism. To study this effect PVA was etched using a 193-nm excimer laser to produce holes. It was found out that lower fluences and lower wavelength helped in producing good quality holes with less thermal damage to the surrounding polymer. Figure 2.6 shows laser-etched holes at 193-nm and 266-nm laser wavelengths.

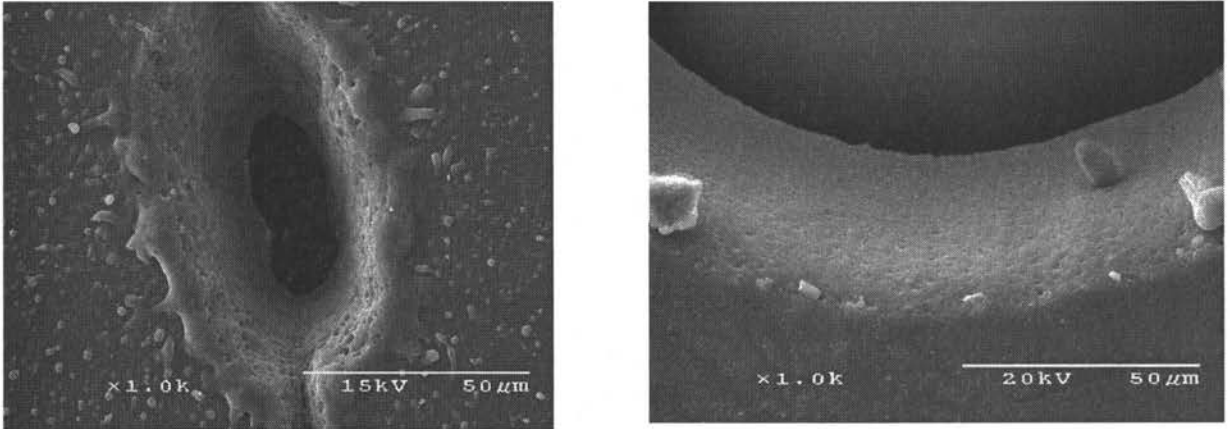


Figure 2.6 266-nm Nd: YAG (left) and 193-nm excimer (right) laser etched holes in PVA.

The repetition rate maintained was 1 Hz and about 100 pulses were required to get through the thickness of the sample ($90\ \mu\text{m}$). The energy above the threshold energy (0.2 mJ-0.5 mJ) did not result in significant removal of the polymer. Higher energy (0.5 mJ to 6.0 mJ) was used in the experiments to achieve through hole. It is observed that as the fluence is increased the hole size increased accordingly. The tradeoff to obtain smaller holes is between the number of pulses and the fluence used. The number of pulses is increased when small fluence is used and vice versa for obtaining good quality holes. In the experiments the hole sizes ranging from $4\ \mu\text{m}$ to $70\ \mu\text{m}$ were observed on the exit of the sample as the energy was increased.

As mentioned above the hole size (diameter) was increasing as the energy was increased, this is due to the Gaussian mode of the YAG laser. Figure 2.7 illustrates the effect of laser energy on the hole diameter.

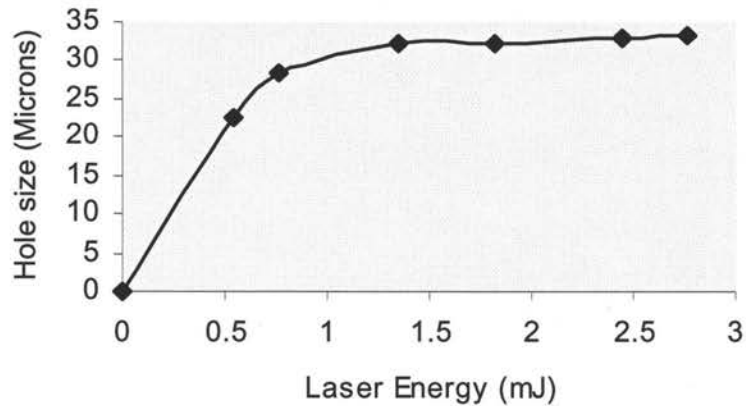


Figure 2.7 Laser energy Vs hole size

The irregularities in the hole shape can be attributed to the spherical aberration and non-circularity of the original laser beam. A microfilter is fabricated with an array of holes. Figure 2.8 shows a part of the filter (at the exit and entry) where the hole sizes varied 40~50 μm (diameter) at the exit. The holes were highly reproducible and were circular at the exit but holes on the entry of the polymers were irregular and thermal damage can be noticed.

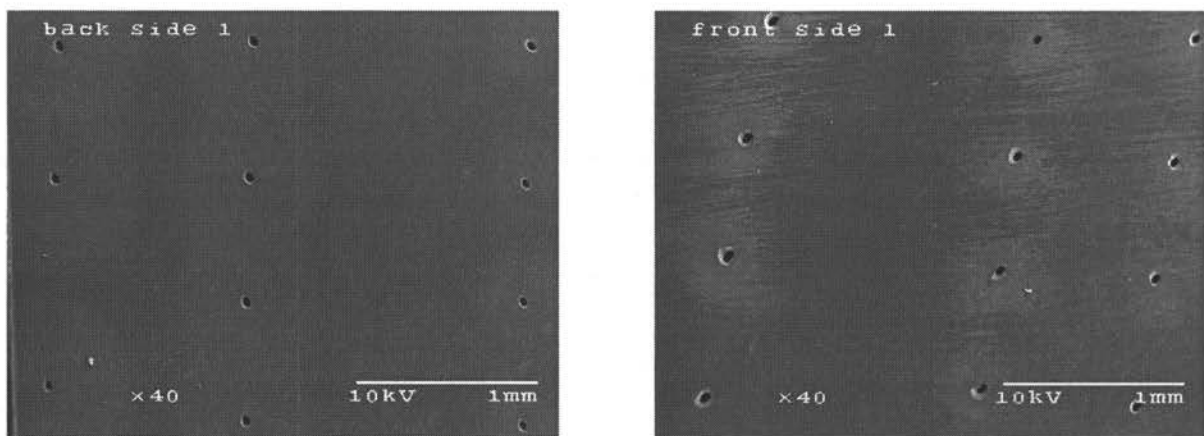


Figure 2.8 SEM image of an array of holes (at the exit)(top) and image of holes at the entry (bottom).

Microchannels:

Microchannels were etched on PVA, PDLA, PCL and PS polymers. Excimer lasers (KrF and XeCl) have been used for this study. The threshold energy for ablating the PVA polymer at 308-nm wavelength was found out to be around 0.5 mJ. It is observed that, below the threshold energy there is no sign of ablation and above the threshold energy there is a linear relationship between the energy and the etching depths for the laser energy used in this study. The experimental etch data of PVA ablated in air at 308-nm wavelength is shown in Figure 2.9 and the absorption coefficient (α) is obtained from the slope of the curve. At 308-nm wavelength, the absorption coefficient was found out to be $0.4 \times 10^4 \text{ cm}^{-1}$.

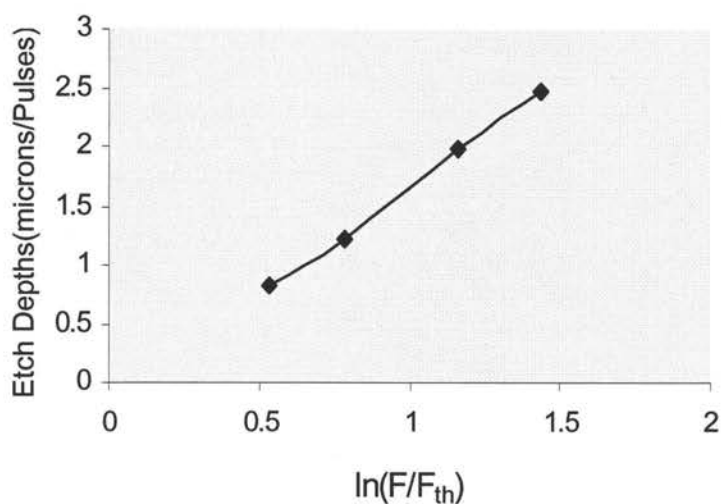


Figure 2.9 Etching depth Vs $\ln(F/F_{th})$ for channels at 308-nm wavelength

Figure 2.10 shows the morphology of the channels etched on PVA at 17 and 22 mJ with 50 pulses respectively. It can be seen that the channels are straight and uniform along the length. Figure 2.10 shows array of channels on PVA at 308-nm.

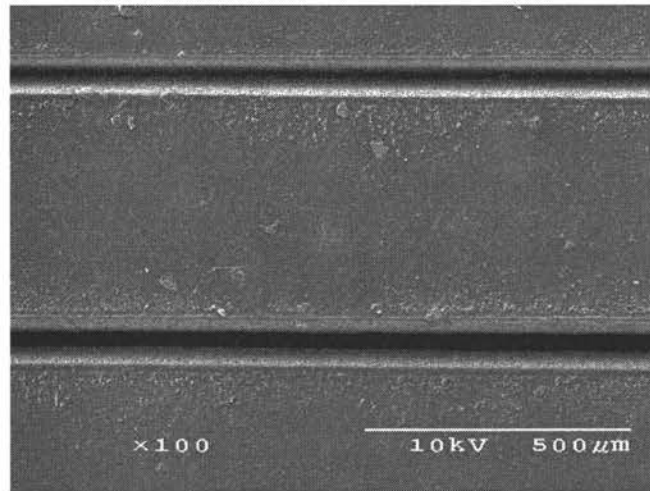


Figure 2.10 SEM image of Microchannels etched in PVA at 17 mJ (top) and 22 mJ (bottom).

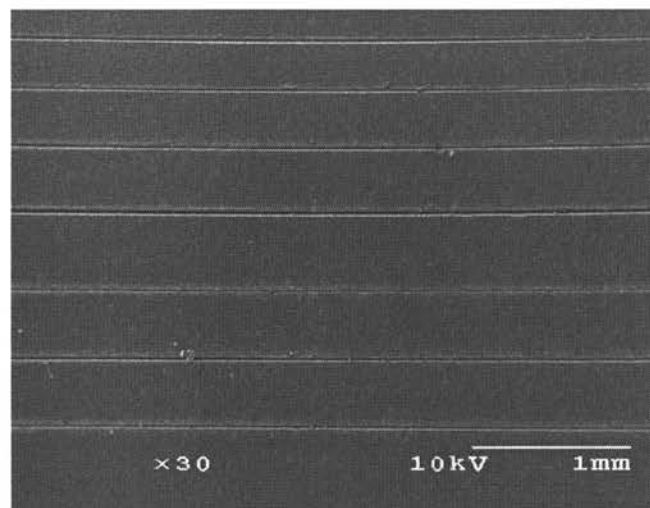


Figure 2.11 SEM image of an array of microchannels etched on PVA at 308 nm.

It is observed that as the energy is increased the channels were wider and deeper. The above figure illustrates the effect of laser energy on the channel dimensions. Since the energy is much more than the energy used for the channel on

the top, the channel on the bottom was wider. The depth of this channel is also more than when compared to the top channel. Distinct edges can be seen and the depth of channels was uniform along the length.

To study the effect of photochemical and photothermal mechanisms on polymers at different wavelengths, PVA has been etched at 193-nm excimer. Channels have been etched in PVA using different parameter and then examined under a SEM for material analysis. Figures 2.12 shows the effect of ablation mechanisms at 308 and 193 nm wavelengths for PVA. It is observed that at 308nm wavelength the effect of photothermal mechanism is very evident. At 308 nm wavelength, the photon energy of light is about 4.02 eV. This energy is not sufficiently high enough to break the polymer bonds, so thermal contribution for ablation plays a role in ablating the material. The energy of photons at this wavelength doesn't completely overcome the energy of the chemical bonds of the polymers. It can be seen that photochemical mechanism is accompanied by the photothermal mechanism by which the polymer is heated, melted and vaporized.

It can be seen from the pictures below that photothermal mechanism dominates at 308-nm wavelength and photochemical mechanism dominates at 193-nm wavelengths. To minimize the thermal effect at 308-nm it is appropriate to etch the polymers at lower energies and less number of pulses.

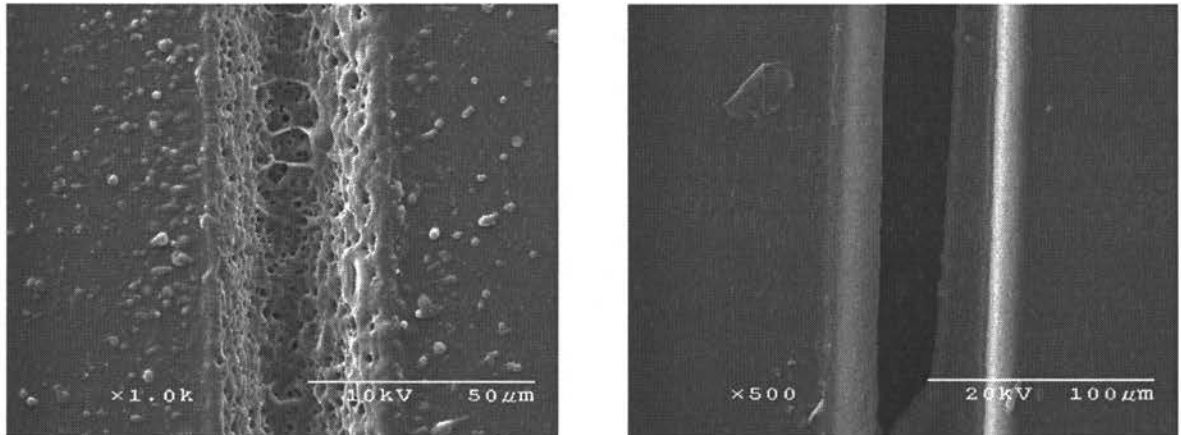


Figure 2.12 Channel etched on PVA at 308-nm wavelength (left) and at 193-nm (right).

PDLA has also been etched at 308-nm and 193-nm to study the ablation effect. It is observed that 193-nm laser has less thermal effects when compared to 308-nm, as the case of PVA. It is also observed that PDLA is tougher to etch than PVA. At same energies PDLA showed lower etch rates and quality of the channels were much inferior to PVA. Figure 2.13 shows channels etched into PDLA at 193-nm and 308-nm excimer lasers. Thermal effects of excimer laser at 308-nm wavelength can be noticed. Localized material deposition is noticed and the number of pulses was minimal (30 pulses). More work needs to be done on PDLA polymer to predict ablation mechanisms compared to PVA polymer. The difference of quality of 308-nm and 193-nm on PDLA can be seen in the figure below.

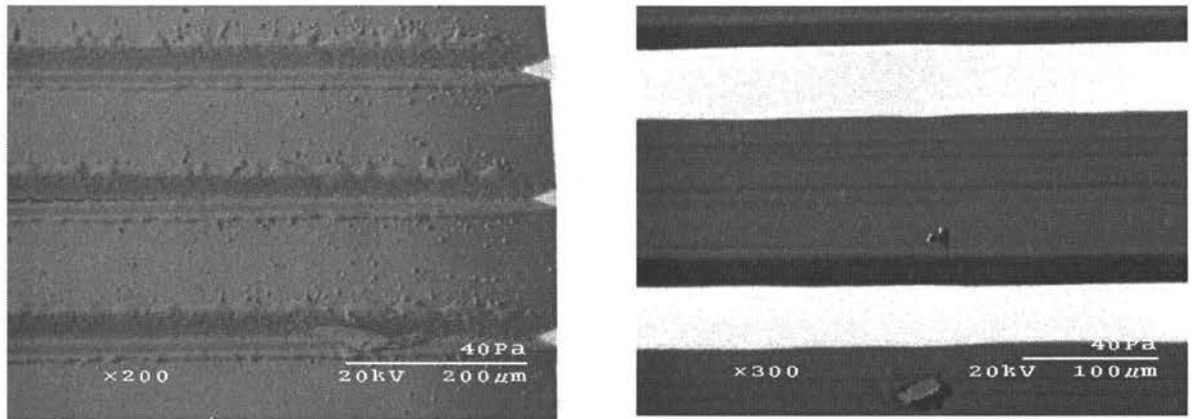


Figure 2.13 Comparison of laser cut quality for PDLA at 308-nm (left) and 193 nm (right).

Polystyrene (PS) and Poly (epsilon-caprolactone) (PCL) are two other polymers used in this study. The quality of laser cuts for these two polymers have been examined using 308-nm and 193-nm excimer lasers. The etching rate and absorption co-efficient at different wavelengths for these polymers have to be studied in the future work. Like both PDLA and PVA these samples exhibited good and quality cuts at 193-nm rather than 308-nm. Figure 2.14 and 2.15 illustrates the effect of wavelength on polymer ablation on polystyrene and PCL respectively.

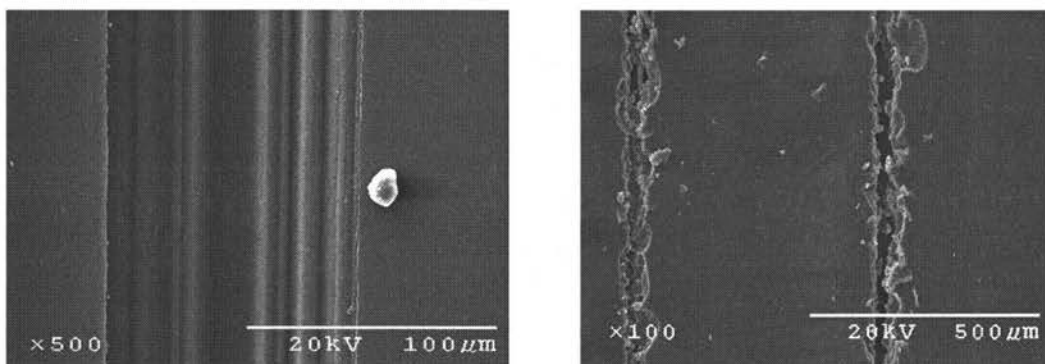


Figure 2.14 Excimer laser cuts in PS at 193-nm (left) and 308-nm (right).

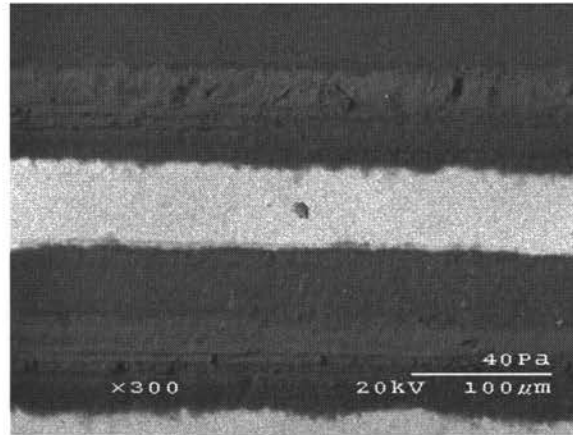


Figure 2.15 Excimer laser cuts in PCL at 193-nm.

It is clearly known that a considerable amount of thermal contribution is accompanied with photochemical mechanism in ablating polymers at 308-nm wavelength. For applications in biomedical engineering, this thermal stress and damage is not accepted. Using a shorter wavelength laser could minimize these thermal effects of ablation. Excimer laser with a wavelength at 193 nm (6.26 eV) or 248 nm (5.0 eV) is a good choice because the photon energy is much larger than the material chemical bond energy. It has been studied and examined for four polymers that as in case of polymers, 193-nm excimer laser is much suited for polymer ablation rather than 308-nm wavelength. Excimer laser is best suited for micromachining channels because of its uniform rectangular beam shape and high photon energies at 248-nm and 193-nm wavelengths.

Summary

Biodegradable polymers have been micromachined by UV laser irradiation for applications in biomedical engineering. An Nd: YAG laser of 266 nm wavelength has

been used to fabricate a biodegradable filter with an array of 5 μm holes to be used for biomolecular separation. Micro channels were produced by excimer lasers finds applications in nerve regeneration. This work on biodegradable polymers for applications in biomedical engineering is first of its kind and it demonstrated that UV laser is well suited for micromachining of biodegradable polymers.

CHAPTER 3

LASER MICROMACHINING OF CERAMICS

In this chapter laser micromachining of Al_2O_3 ceramics is studied using 266-nm frequency tripled Nd: YAG laser and 193-nm excimer lasers. Microholes and microchannels are patterned on ceramics. Microholes patterned are used for interconnects between the multilayer chip modules and microchannels serves purpose in ceramic micro fluidic devices. The experimental results of micromachining fired ceramics and green ceramics are reported.

INTRODUCTION

Ceramics are one of the important MEMS packaging materials currently being used to fabricate many microdevices. The introduction of these materials in MEMS fabrication makes it easy to fabricate 3-D meso or large-scale devices at a cheaper cost. Ceramic hybrid electromechanical systems (CHEMS) are finding new applications to overcome the disadvantages associated with the conventional silicon MEMS devices. To support the rapid advancements in this field it is necessary to introduce innovative techniques to process ceramics, which are hard and brittle materials.

New lithographic, deposition, and etching tools for micro fabrication on planar silicon substrates have led to remarkable advances in miniaturization of silicon devices. However silicon is often not the substrate material of choice for applications

in which there are requirements for electrically or thermally insulating substrates, low capacitance, and resistance to corrosion, or hermetic sealing (Tan, 2000). Packages on which chips are mounted for connection to other devices have to keep pace with the rapid advances made in ICs. So speed, power, and area should not be compromised. Small distances between chips and shorter interconnection distances are of great importance for faster operations. In multilayer sandwiches, blind via holes provide high-speed connections between surface-mounted components on the board and underlying layer (Zsolt, 2000).

Early fabrication methods in fired ceramics involved machining substrate features with carbide, diamond or ultrasonic tools. These techniques are not cost effective and were limited in the type and size of features they could create (Rong, 1990) and are very time and cost consuming. As feature sizes fall below one thousandth of an inch, mechanical approaches to drilling, engraving and shaping these hard and brittle materials must be replaced with photon or particle beam techniques. The requirement for material processing with micron or submicron resolution at high speed and low cost is fundamental and special tools are needed for this work, and lasers can play an important role.

Laser cutting and drilling of ceramics is a promising and interesting field. The main advantages are high flexibility in producing complex shaped parts and the absence of mechanical loading during the process (Chryssolouris, 1991). The most critical point to note while machining ceramics is the crack formation. These cracks reduce the strength and are very critical for crack growth formation, which will

ultimately result in the part failure. It is necessary to choose the laser machining parameters for processing these hard and brittle materials to avoid the crack formations.

Drilling of small holes in unfired, fired ceramics is very important in microelectronic applications. The wavelength of the laser beam is an important parameter while processing materials. Since the applications in microelectronics are on the order of microns it is necessary to choose the appropriate wavelength for the applications. Shorter wavelengths have high photon energies and high pulse peak powers that result in direct evaporation of the material and hence less heat affected zones. Figure 3.1 represents the relation between the wavelength and absorption properties of ceramics and other materials.

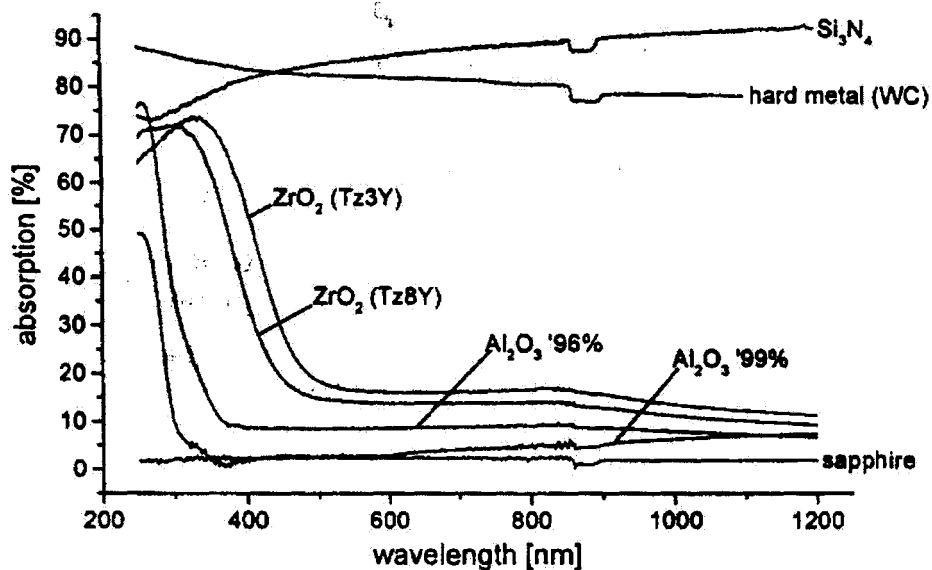


Figure 3.1 Relation between wavelength and absorption properties for ceramics.

For processing ceramics the fundamental wavelength of Nd: YAG laser (1064-nm) is not appropriate because most of the ceramics are not good absorbers at this wavelength. At this wavelength, the smallest size of the features is limited and high energies are required. Shorter wavelengths and pulse-widths is the key to attain features on the micro scale (Kunz et al, 1994). Excimer and frequency multiplied Nd: YAG lasers offer shorter wavelength and pulse widths in the order of 6-10 ns and are suitable for processing these materials on the micro scale. UV light gives cleaner edges than those obtained from visible or IR machining and the TEM00 beam profile of Nd: YAG allows drilling of sub-micron holes.

As the demand for smaller manufactured structure increases, the techniques for efficient and economical laser micromachining continue to draw more attention. The work reported here investigates the micromachining of MEMS packaging materials such as ceramics. Fired and green Al_2O_3 was used in the study. Micro holes are drilled in ceramics and polymers to provide interconnects between different layers of multichip modules and micro channels are drilled in ceramics for applications in ceramics fluidic devices.

Theoretical Background

UV laser etching of Al_2O_3 ceramics has been the subject of numerous studies. The volume of ceramic that can be removed in each pulse is strongly fluence dependent and the fluence is typically several times the threshold fluence (Duley, 1996). Various research groups have done etching of Al_2O_3 by using different laser sources. Most work in ceramics has been done in evaluating the laser material

interactions and surface morphology after the machining process (Hourdakis et al, 1991) but very little work has been done in applying laser micromachining of ceramics for applications in microelectronic packaging. A summary of the previous work on micromachining ceramics is discussed.

Some of the considerations taken while machining ceramics with lasers are the threshold intensity, material resolidification and crack formation. Laser drilling of ceramics requires high energy to initiate drilling of holes. A threshold energy density is defined as the energy density level below which material removal is not possible. Coating the ceramic with a thin layer of conducting material can reduce this threshold energy. One problem encountered in ceramic drilling is resolidified of the material, which forms in the hole. The melting temperatures for ceramic materials are high and the material removal process preliminarily occurs due to melting and a molten layer is formed at the erosion front. Due to the limited space in the hole (in the order of microns), driving away the molten material with a gas jet is difficult. The remaining recast layer reduces hole depth by absorbing beam energy and degrades surface quality by increasing hole surface roughness. Micro-crack formation near the drilled hole is another problem encountered in laser drilling of ceramics. Rapid heating during laser processing induces cracks, which causes large temperature gradients near the hole surface. Preheating the workpiece to an elevated temperature prior to laser machining can minimize microcracking. By preheating the, temperature gradients achieved during laser machining will be reduced significantly compared to laser drilling of a cold workpiece.

The thermal nature and interaction of the radiation with the material, thermal stresses and distortion cannot be avoided when using lasers in the IR region of the spectrum (Nikumb, 1994) to process ceramics. Intense UV lasers are predominantly electronic in nature and are apt for ceramic materials for producing fine features and good quality finish. Oliveira et al (1998) has reported the ablation mechanisms involved in laser micromachining of Al_2O_3 - 34%wt TiC ceramic composites. The Al_2O_3 - TiC ceramic composites have been etched to study the surface topography and structure of the composites after irradiating with a 248-nm KrF excimer laser. Laser cutting of oxide and non-oxide ceramics had been investigated by Hans et al (1994) by using a 1500 W CO_2 laser and 500 watt pulsed Nd: YAG laser and found that the crack formation while cutting the ceramics was less observed than that of the continuous wave mode. Gower (1993) reported extensive data on the threshold fluence and etching rate for Al_2O_3 ceramics for excimer wavelengths at 193, 248 and 308 nm. It was reported (Lowndes et al. 1993) that at relatively lower fluence the surface of Al_2O_3 ceramic can be melted causing a glazing surface layer, increase in grain size, reduction in porosity and density of microcracks and decrease in surface roughness.

Materials and Procedures

Ceramics are composed of both metallic and nonmetallic atomic species. Many of the ceramics are crystalline and mostly the nonmetal component is oxygen, nitrides or carbides. Al_2O_3 , MgO, CaO, AlN, BN, Si_3N_4 , SiC are some of the typical ceramics. The ceramics have covalent/ionic bonds and hence there are no free

electrons unlike metals. Hence ceramics are generally poor conductors of electricity and are used as insulators in electrical applications. Ceramic materials are intrinsically stronger than metals but ceramics tend to fracture in a brittle manner. This brittleness generally limits their use as structural materials. Some of the properties of Al_2O_3 ceramic used in this study are listed in Table 3.1.

Table 3.1 Properties of Al_2O_3 ceramic

Properties	Wavelength (nm)	Value
Refractive Index	248	1.846
	266	1.833
	308	1.811
Density (g/cm^3)		3.99
Melting Point (C)		2050
Molecular weight		101.96
Thermal conductivity (w/Mk)		~12-46
Specific Heat (J/kgK)		~750-1225
Young's Modulus (Gpa)		3450
Bulk Modulus (Gpa)		250
Shear Modulus (Gpa)		145

Their rigid bond structure offers advantages such as high temperature stability, resistance to chemical attack, and resistance to absorption of foreign substances. Some of the common applications of ceramics are in electronics, piezoelectric devices, medical implants, high temperature engineering, chemical engineering, and the recent developments in ceramic hybrid electromechanical systems (CHEMS) and in ceramic multichip modules (Ceramic MCM). The Al_2O_3 ceramic is extremely superior in abrasion resistance, and also has the properties of heat resistance and chemical resistance and electric insulation and hence widely used due to its excellent cost performance.

The experimental setup used in Chapter 2 (Figure 2.3) is used for micromachining ceramics. All the experiments are carried out in air for fired and green ceramics. The procedure for these experiments is listed below.

1. Set the laser energy constant
2. Set the pulse repetition rate to 10Hz
3. Open the coolant flow
4. Warm up the laser for a couple of minutes by blocking the pulses (15 minutes)
5. Fix the samples to the x-y stage firmly
6. Move the stage to position the sample near the beam
7. Measure the energy of beam
8. Shape the beam and focus it through a focussing lens

9. Start the ablation process
10. Run the ablation for required number of pulses
11. Block the laser light

Typically the above steps are followed in the experimental procedure while machining the ceramics. The etch depth per pulse is later calculated by dividing the total etch depth by total number of pulses delivered. The experiments are repeated by controlling the parameters such as laser energy, number of pulses, pulse repetition rate etc to obtain the required features. The etch depths are obtained by using a surface profilometer and are observed under a scanning electron microscope (SEM) to study the surface modifications and morphology after the laser ablation experiments.

Results and discussion

Preliminary study has been done on the ablating Al_2O_3 by UV irradiation. Microholes and microchannels are etched on fired ceramics. The surface morphology and the ablation rate at various energies and pulses are studied.

Microholes were etched by ArF excimer laser and Nd: YAG laser to study the wavelength affect on the ablation. It is observed that during the first pulses of ablation a thin layer of the ceramics is melted first and then the ablation process is dominated by vaporizing the bulk of material. Redeposition of the ceramic can be seen in the picture, this is because the hole is small and no gas was used to flush out the debris. The irregular shape of the hole is due to the bad beam shape. Holes

were drilled at higher energy where deeper holes were achieved. To study the effect of energy on the ablation the energy and the number of pulses for drilling were increased. All the experiments were carried at 10 Hz and at 18 mJ energy no cracks in the ceramics were found near the machined features. Heat affected zone was observed around the drilled holes in the form of darks rings. Figure 3.2 shows a hole drilled at 18 mJ at a) 1000 pulses, b) 1400 pulses, c) 2000 pulses Nd:YAG laser.

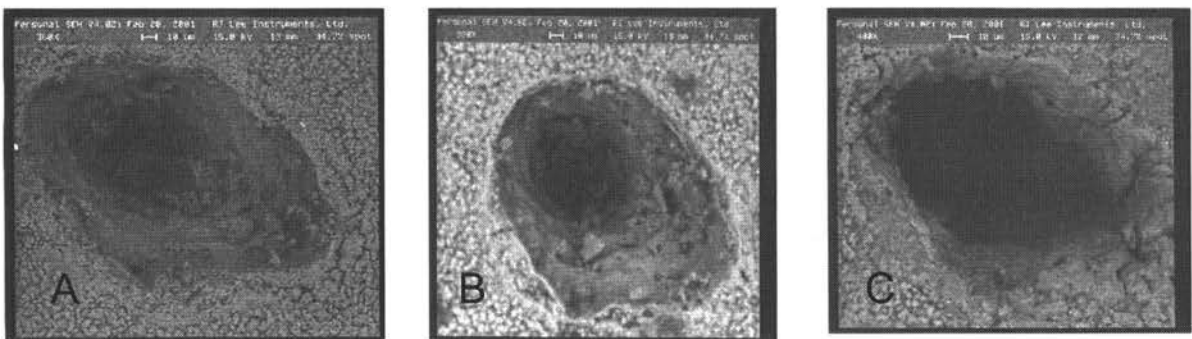


Figure 3.2 Holes etched at 18 mJ for a) 1000 b) 1400 pulses and c) 2000 pulses

Dark marks (HAZ) are noticed around the edges of the holes caused by plasma heating of the surface and particle redeposition is seen in the figures. As the energy is increased the HAZ was more prominent since larger plasma plume was produced. To study the effects of wavelength on ceramic ablation ArF excimer (193-nm) laser was employed to etch the ceramics.

The KrF laser produced a maximum of 4 mJ of energy, with repetition rate of 10 to 100 Hz. The experiments were conducted at 10 HZ frequency and at highest energy. An array of holes has been drilled for 2000 pulses. The holes measured 60 microns in diameter.

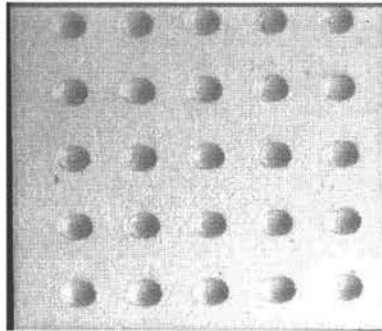


Figure 3.3 shows array of holes etched in ceramics.

Microchannels were etched in using the ArF laser. The cylindrical lens used in the experiments produced straight channels and small cracks are observed along the length of the channels. Small globular structures are observed and the growth of this laser modified surface layer along the length affects the ablation rate. Material deposition has also been observed. The energy used was 4 mJ and a repetition rate on 10 Hz was used. The channels measured less than 10 microns in width and depth. A train of 2000 pulses has been targeted at the sample. Figures 3.4 and 3.5 illustrate the SEM micrographs of the channel and array of channels in ceramics respectively.

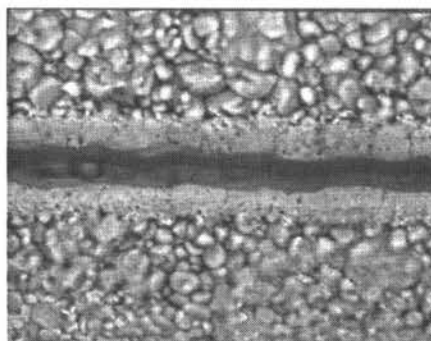


Figure 3.4 Microchannel etched at 193-nm laser wavelength

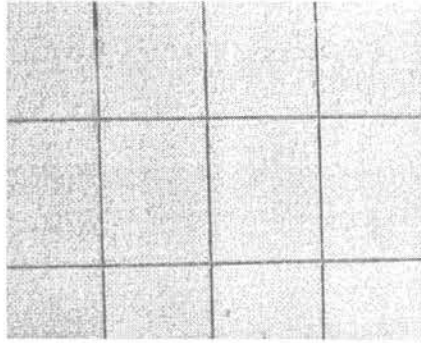


Figure 3.5 Array of channels etched at 193-nm laser wavelength

Summary

MEMS packaging materials such as ceramics have been micromachined for applications in microelectronics and multichip modules. Al_2O_3 ceramic has been micromachined for these applications with UV Nd: YAG and Excimer lasers. Holes have been drilled in this insulating material that find applications in high density interconnect circuits. Microholes drilled were 60 micron in diameter. Micro channels have also been patterned on both those find applications in ceramics microfluidic devices and other devices. An ArF excimer laser has been used to create tiny channels as small as 10 microns wide and 10 microns deep. This work on ceramics demonstrates that UV laser is the tool for machining features on the micron scale.

CHAPTER 4

CONCLUSIONS

Conclusions of present work

Laser micromachining of biodegradable polymers was performed in air using excimer and Nd: YAG lasers. PVA, PDLA, PS and PCL are of the biodegradable polymers used in this study. UV laser percussion drilling is performed with frequency quadrupled Nd: YAG laser at 266-nm wavelength. The rectangular beam profile of the 308-nm XeCl and 193-nm excimer lasers were used to etch microchannels on these polymers. This research work of laser micromachining of biodegradable polymers for applications in biomedical engineering is first of its kind and it is showed that lasers are efficient and suitable for processing biodegradable polymers on the microscale. The results and conclusions for this work on polymers are as follows:

1. Microholes drilled in polymer PVA were 5 μ m in diameter and a filter was fabricated with an array of holes for bimolecular separations.
2. Microchannels etched for applications in artificial nerve regeneration were 20~40 μ m wide and depth of the channels can be controlled with sub-micron resolution.
3. The etching depths per pulse were calculated for the polymers and plotted against the fluence.
4. The absorption coefficient for the polymers is found out by applying the Beer Lambert's law at different laser wavelengths.

5. Thermal effects on the polymers were predominant at 308-nm wavelength than at 266-nm wavelength and 193-nm wavelengths.
6. As the fluence is increased the size of features increased and thermal damage was also noticed around the machined features.

Laser micromachining of Al_2O_3 ceramics was performed in air using 266-nm and 193-nm excimer lasers. Hole drilling and patterning of microchannels was studied on fired ceramics. This work is aimed at drilling microholes on ceramic substrates for applications in microelectronics and for via interconnects. Microchannels find applications in ceramic microfluidic devices. The results and conclusions for this work are:

1. Microholes drilled in ceramics produced cracks and the hole was irregular in shape due to the bad beam shape.
2. Resolidification and redeposition of the ceramic material was observed on the walls of the holes.
3. HAZ was observed around the edge at the entry of the holes.
4. The microholes etched were 60 μm in diameter.
5. The microchannels etched were very narrow and deep in the order of 8~10 μm .

Recommendations for future work

Biodegradable polymers are finding new applications, and an efficient way to process these materials by lasers is of high interest. The current work on polymers

at 193-nm, 266-nm and 308-nm exhibited photothermal and photochemical effects on the polymer. To utilize the full potential of the photochemical mechanism in ablating the polymer shorter UV laser wavelengths such as 157-nm could be used. Processing these materials could also be examined using Ultrashortshort picosecond (10^{-12} s) and femtosecond (10^{-15} s) pulses. The effect of biodegradability on the polymers after laser etching could be studied. Lots of work has been done on processing materials on the microscale but a very few work is done in the nanoscale length regime. Nanotechnology holds huge potential applications in the future and lasers can play an important role. The future work could concentrate on producing features on the nanoscale. Since conventional laser methods are not suitable to realize nanostructures or nanopatterns due to diffraction limit the wavelength, techniques such as near field technology could be utilized to conduct work on the nanoscale.

More work can be done on the ceramics by shaping the beam to get good quality holes. Lasers with high power and shorter wavelengths such as 193-nm, 248-nm and 266-nm could be used to study the effects of laser wavelength on the machining process.

APPENDIX A

SCANNING ELECTRON MICROSCOPE

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. The SEM gives information on topology, morphology, composition and crystallography of the samples. It has a large depth of field, which allows a large amount of the sample to be in focus at one time and also produces images of high resolution. Preparation of the samples is relatively easy since most SEMs require the sample to be conductive. If the samples are not conductive (ceramics, plastics etc.) a thin layer of conductive material is applied to the samples in a sputter coater. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

The development of the Scanning Electron Microscope in the early 1950's brought with it new areas of study in the medical and physical sciences because it allowed examination of a great variety of specimens. Specimens such as metals, ceramics, polymers, human hair, fingernails, biological samples etc. have been examined under the SEM.

When a SEM is used, the column must always be at a vacuum. If the sample is in a gas filled environment, an electron beam cannot be generated or maintained because of a high instability in the beam. Gases could react with the electron source, causing it to burn out, or cause electrons in the beam to ionize, which produces random

discharges and leads to instability in the beam. The transmission of the beam through the electron optic column would also be hindered by the presence of other molecules. Those other molecules, which could come from the sample or the microscope itself, could form compounds and condense on the sample. This would lower the contrast and obscure detail in the image.

A vacuum environment is also necessary in part of the sample preparation. One such example is the sputter coater. If the chamber were not at vacuum before the sample is coated, gas molecules would get in the way of the argon and gold. This could lead to uneven coating, or no coating at all.

The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses that focus and direct the beam down towards the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.

APPENDIX B

SURFACE PROFILOMETER

The surface profilometer is a very delicate instrument that measures the surface profile by scanning a mechanical stylus across the sample. The profilometer can be used to measure etch depths, deposited film thickness and surface roughness. A flat surface with well-defined step is required to generate a good profile for a step height measurement.

The flat sample is placed on the X, Y, Z table and the sample is made to touch the mechanical stylus as a preliminary step for scanning the sample. The instrument is connected to a digital Interface readout and a strip chart recorder. The stylus scans across the sample and the surface profile is traced out onto the strip chart recorder. Some of the systems have vertical ranges from 1000Å to 1000kÅ with a resolution of 50 Å.

The samples that are to be examined under this instrument should be flat, clean and usually hard substrates such as silicon wafers and glass slides. Care should be taken when scanning soft materials such as polymers, green ceramics etc, Where the stylus might etch these materials and lead to faulty results.

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