1-1-2009

Two-photon polymerization using femtosecond laser

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TWO-PHOTON POLYMERIZATION USING FEMTOSECOND LASER

by

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B.E. (Mechanical Engineering)

Ryerson University (Canada), 2006

A Thesis

presented to Ryerson University

in partial fulfillment of the requirement for the degree of

Master of Applied Science

in the program of

Mechanical Engineering

Toronto, Ontario, Canada, 2009

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ABSTRACT

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The demand for microfabrication by laser technology has been the foundation of the new age of three-dimensional micro-structuring processes. One of these new processes that has been established in recent years has been the two-photon polymerization (2PP) technique by femtosecond lasers. Unlike the well known stereo-lithography (SL), this newly developing technology provides simple and rapid fabrication procedures and demonstrates much better quality and structural resolution. In addition, by using computer generated 3D models, this technique can produce any kind of 3D structures that can be then fabricated and integrated into complicated devices. Currently used strategies and methods to produce the smallest possible feature by using 2PP process are acceptable but the strive for enhanced results is necessary in order to continue the progression of such technique

This thesis proposes a broader knowledge on laser parameters that affect 2PP process and the implementation of such parameters in order to produce the smallest feature size and the highest aspect ratio structure possible. A high repetition rate, high power femtosecond laser is investigated for exceeding the quality demand established by the current market. An experimental study of the proposed laser system and the analysis of control parameters, such as laser power and repetition rate, are presented. The influence of pulse width, laser power, substrate material, and scanning speed on aspect ratio is analyzed in detail. The produced micro-

structure with the measured aspect ratio indicates the capability of meeting the quality and requirements that have been established by the current market.

Acknowledgments

I would like to thank my research supervisors Dr. K. Venkatakrishnan and Dr. B. Tan, for their enormous supervision and guidance. Sincere gratitude to both of my supervisors for their support and sense of direction that made it all possible.

I would like to thank Dr. Greg Kawall, Director of Mechanical Engineering Graduate program, all the faculty members, technical officers and administrative staff members for their kind support and cooperation all the time during my stay at Ryerson University.

I am also grateful to my family for their continued support, prayers and love. Deepest gratitude to my father and mother, who were there to support me through both the hardship and contentment

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Nomenclature

1PP	Single Photon Polymerization
2PA	Two-Photon Activated
2PP	Two-Photon Polymerization
2D	2 Dimensional
3D	3 Dimensional
CAD	Computer-Aided Design
CD	Critical Dimension of printed structure size
DOF	Depth of Focus
MEMS	Micro-Electro-Mechanical Systems
NA	Numerical Aperture
NIR	Near Infrared
SEM	Scanning Electron Microscope
SL	Stereo-lithography
TPA	Two-Photon Absorption
PI	Photo Initiator
UV	Ultra violet
CAD	Computer-Aided Design
CD	Critical Dimension of printed structure size
DOF	Depth of Focus
KHz	Kilohertz (10^3 Hz)
MEMS	Micro-Electro-Mechanical Systems
MHz	Megahertz (10^6 Hz)
NA	Numerical Aperture
NIR	Near Infrared
SEM	Scanning Electron Microscope
SL	Stereo-lithography
TPA	Two-Photon Absorption
PI	Photo Initiator
UV	Ultra violet
W	Watt

ns	Nanosecond (10^{-9} s)
fs	Femtosecond (10^{-15} s)
mm	Millimeter (10^{-3} m)
μm	Micrometer (10^{-6} m)
nm	Nanometer (10^{-9} m)
mW	Milliwatt (10^{-3} W)
ps	Picosecond (10^{-12} s)
D_0	Spot size diameter
D	Laser beam diameter
d	Voxel size
f	Focal Length
h	Planck's constant
I*	Intermediate state of the photo initiator
L	Pixel length
M	Monomer or oligomer unit
M_n	Macromolecule containing n monomer units
PhCs	Photonic crystals
q	Order of multi photon process
R•	Free radical,
R+	Reactive cation
r	Radius of the lens
Ti	Titanium
v	Lightwave frequency
Yb	Ytterbium
λ	Exposure Wavelength
λ_0	Wavelength of the laser
ρ	Density

CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION TO POLYMERIZATION

Polymerization is essentially the addition of smaller molecules, varying in size, that form a larger structure which is composed of three-dimensional network of chains. This process can be divided into two different categories: addition polymerization (chain growth) and condensation polymerization (Step growth). Addition polymerization occurs when monomers, which are small single molecules, remain structurally unchanged and are linked together by double and triple chemical bonds. The polymerization of vinyl chloride is distinctive application of addition polymerization. Typical vinyl chloride molecules contain two carbon atoms, three hydrogen atoms, and one chlorine atom [1]. One of the chemical characteristics of carbon is that each carbon atom usually forms four covalent bonds and in this case, a double bond between the adjacent carbon atoms. During free radical polymerization, one of the two bonds between the two carbons ruptures, leaving behind one unshared electron on each carbon atom. In general, an atom with an unpaired electron is very reactive. As a result, addition polymerization is also sometimes called free radical polymerization. If two such free radicals meet, they can form a "dimer", which is simply a combination of two monomers bonded together, with a new covalent bond linking the two vinyl chlorides as illustrated in Figure 1-1 [2].

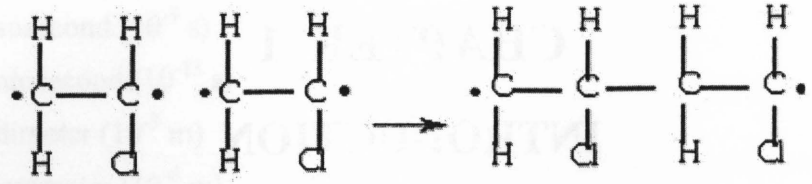


Figure 1-1: Vinyl chlorine free radical

This dimer can react with another vinyl chloride to form a three bonded vinyl molecule called a trimer. By repeating this process many times over, a long polymer with hundreds or even thousands of monomer units long can be formed. This end result polymer is then called polyvinyl chloride.

On the other hand, condensation polymerization transpires in a polymer through a chemical reaction that is smaller in size than the two or more monomers that were joined to form it. This fact occurs due to the elimination of small molecules, such as hydrogen chloride and water, during the synthesis of a polymer. In condensation polymerization, covalent bonds are rearranged in such a way that two monomers, unspecified elements "X" and "Y" as shown in Figure 1-2 [2], are connected and H_2O molecule is diluted out. Both molecules have OH atom connected to another element. In this reaction, the bond between X and OH is broken in one molecule and the bond between O and H is broken in the other. As a result, two new molecules are formed with one being the water formed by the OH from XOH and the other H from HOY. Furthermore, the new molecule consists of two monomers with the remaining O atom forming a bridge between X and Y [3].

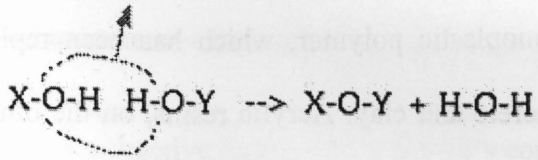


Figure 1-2: Illustration of condensation polymerization reaction is shown with water being condensed out of the two reacting molecules

One example of such a polymerization technique is the curing of concrete. The chemical reactions that occur in the curing of mortar or of concrete are complex but condensation plays an important feature. Cement is a material that when mixed with water, holds aggregates such as sand and pieces of rock or gravel together. Furthermore, cement also contains silicates, which are minerals that contain some form of the silicate anion and various cations (e.g., calcium, sodium, magnesium, iron, aluminum ions). A simple silicate anion is contains four oxygens that each form a covalent bond to an atom of silicon. The structure is like a triangular pyramid structure with silicon in the very center and with oxygen present at each vertex. In the presence of water, silicates become hydrated and some of the oxygen atoms form a covalent bond with a hydrogen nucleus from the water molecule. Since the hydrated silicates contain Si-O-H bonds, condensation becomes possible [3].

The main difference between the two classes of polymerization can be portrayed by the amount of change that the monomers endure through bonding. The way that the monomers combine also plays a vast role in the distinction between the two principles. In addition polymerization, which is the simplest, merging of monomers happens at a single rate in which one monomer is added at one time while condensation polymerization results through accumulations of monomers at various times. The main area of application of such processes is the manufacturing of high polymers such as: Polyvinylchloride (PVC), Low density polyethylene

(LDPE), ethylene vinylacetate copolymers (EVA), styrenic polymers, and acrylic resins [4]. PVC is a widely used thermoplastic polymer, which has been replacing traditional building materials such as wood, concrete and clay. Acrylic resins, on the other hand, play an essential part of decorative, automotive, car refinish and wood coatings. Other applications of this group of polymers include the use as adhesives and toner resins.

In general, the process of polymerization induces the formation of stable covalent chemical bonds between the monomers that sets it apart from other processes. All polymerization reactions tend have a similar processing pattern by having small molecules combining to form larger ones. As a result, the fabrication of micro features becomes virtually impossible by implementing such a technique.

1.2 PHOTO POLYMERIZATION

Photo polymerization refers to the process of using light as an energy source to induce the conversion of small unsaturated molecules in the liquid state to solid macromolecules thorough polymerization reactions. Photon polymerization deals with those processes that are induced by light in the ultraviolet, visible to infrared spectral region. The basic components of the starting liquid material are monomers and oligomers [5]. Upon light excitation, the monomers or oligomers may be solidified by two means: polymerization and cross linking. An important feature of polymerization is the chain reaction by which macromolecules are created, while cross-linking is concerned more with the formation of cross links with chemical bonds rather than entangling of polymer chains. A single photon polymerization process consists of the following steps [5]:

$$h\nu\text{UV} + \text{initiator} \rightarrow \mathbf{R\bullet} \text{ or } \mathbf{R+} \qquad \textit{Eq. 1-1}$$

$$\mathbf{R\bullet} \text{ or } \mathbf{R+} + \text{monomers} \rightarrow \text{free radical or cationic polymerization}$$

Where R• is a free radical, R+ is a reactive cation, *h* is a planck's constant, and *v* is the lightwave frequency. In a single photo polymerization process, an initiator, which is an ingredient that absorbs light and is responsible for the production of free radicals in a free radical polymerized system, only absorbs one ultraviolet (UV) photon with a short wavelength through linear absorption. This process deals with those materials that are induced by light in the UV, visible to IR spectral region.

There are a lot of well-known applications for a single-photon polymerization (1PP) like UV photolithography or stereo-lithography, where a single ultraviolet photon is needed to initiate the polymerization process near the surface of a photosensitive resin. Depending on the concentration of photo initiator of optionally added absorber molecules, the ultraviolet light is absorbed by the resin within the first few micrometers. As a result, single photon polymerization is a planar process restricted to the surface of the resin [6].

In addition to its indispensable role in microelectronics and optoelectronics, photolithography has been widely utilized for versatile fields including MEMS, micro sensors and actuators, micro-chemical reactions and analytical systems, and micro-optical systems. Currently UV lithography has feature sizes down to 250 nm, and it is expected to be reduced to around 100 nm in the near future by use of a combination of deep UV light and improved photoresists. To push the resolution of conventional lithography into the sub-100 nm regime, new irradiation sources with short wavelengths have been utilized, including: soft X-ray lithography, e-beam writing, atom beams, focused ion beam (FIB) writing, and proximal-probe

lithography. Better resolution, up to several nanometers has been achieved by some of these technologies. However, substantial efforts are needed to improve the development of reflective optics and new types of masks, and arrays of beams. In addition, all of these systems need to operate in vacuum, which causes high costs, difficult maintenance, and low fabrication efficiency [5].

Another application of a single photon polymerization technique is soft lithography. It includes microcontact printing (mCP), embossing, microtransfer molding, cast molding, injection molding, and replica molding. All of these processes have a common feature. They all use elastomer, typically PDMS or thiol, patterned from a master plate created by lithography, as the stamp, mold, or mask to generate micropatterns and microstructures. This technology circumvents the limit of optical diffraction and achieves resolution up to 20 nm. In addition, soft lithography, which is different from lithography by being intrinsically suitable for use on planar structures, can be feasibly used to produce surface structures of different heights [5].

1.3 TWO-PHOTON POLYMERIZATION

An alternative approach to the rapid and low-cost fabrication of nanostructure surfaces is the application of 2PP. Selection rules for single-photon and two-photon excitation (TPE) are different but most resins that polymerize under UV exposure can undergo similar reactions when two photons are absorbed simultaneously provided that the light intensity is large enough.

In the 2PP process, the following step, which only differs in the initial stage of the reaction from a single photon polymerization, is implemented [5]:

$$2h\nu\text{NIR} + \text{initiator} \rightarrow \mathbf{R}\bullet \text{ or } \mathbf{R}+ \qquad \textit{Eq. 1-2}$$

In this process, an initiator absorbs two near-infrared (NIR) photons with a long wavelength through non-linear absorption. In this technique, two-photon absorption is used to expose a photoresist's one volume element (voxel) at a time. The voxel is best regarded when it is spherical in shape (L/d ~ 1), where L is pixel length and d is voxel size. Since voxel shape affects resolution limits, it becomes an important factor in the 2PP process.

In general, two-photon polymerization, which will be discussed in more detail later in the thesis, is the most highly developed multi-photon absorption technique.

1.4 1PP AND 2PP COMPARISON

A very important distinction between two-photon polymerization and lithography technique is that in the case of two-photon polymerization, near infrared laser pulses are used for curing of photosensitive materials. Near infrared light can be focused into the volume of the ultraviolet-sensitive resin and can therefore be used for truly three-dimensional structuring. On the other hand, in the case of the lithography technique, ultraviolet laser radiation is implemented. Since photosensitive materials are usually transparent in the infrared range and are highly absorptive in the ultraviolet range, 2PP can be initiated with infrared laser pulses within the volume for fabrication of three-dimensional structures, whereas 1PP occurs at the surface due to single photon absorption.

In single photon multi-beam interference, the limiting factor of the achievable thickness is the power attenuation due to the linear absorption of resins. On the other hand, two-photon polymerization can record deeper due to its penetration capability, but this merit is counteracted by the short coherence length. A solution to this problem is the use of picosecond lasers, which

have coherence lengths of the order of millimeters, and their transient high power should still be sufficient to launch 2PP process [7].

However, it is important to understand that both 1PP and 2PP processes are used for the purpose of micromachining. The only difference between the two techniques remains that by using the 2PP approach, femtosecond lasers enable microfabrication with resolution beyond the diffraction limit. As a result, 1PP is a planar technology technique with layer-by-layer polymerization steps while 2PP is truly a three dimensional high-resolution technology [8].

Another major issue is that two-photon polymerization uses a wavelength double that needed for linear absorption. Two-photon polymerization is helpful in reducing holographic line width, but the doubled wavelength becomes a detrimental factor in reducing the structure periodicity. The spatial distribution of the square of light intensity is steeper than that for the light intensity itself. Therefore two-photon polymerized structures are relatively easy to develop due to a sharper contrast between the maximum and minimum of polymerization. To use this advantage, a picoseconds pulse at visible wavelength range may be a good choice for two-photon lithographic recording [7].

1.5 APPLICATIONS OF 2PP

1.5.1 PHOTONIC CRYSTALS AND WAVEGUIDE STRUCTURES

Photonic crystals (PhCs) are microstructures consisting of spatially alternating regions with different dielectric constants. These constants act in fact as refractive indices. Propagation of light inside a certain frequency range, called photonic band gap (PBG), is forbidden in such structures. The frequency region that results in PBGs is the product of multiple interferences

among waves scattered from each primitive unit [9]. The only way that 3D photonic crystal can occur is when the dielectric constant periodicity occurs in all directions. Depending on the topology and dielectric constant contrast of photonic crystals, their optical properties can be modified in a desired manner. As a result, these features provide the option of creating many fascinating applications of photonic crystals such as: control of spontaneous emission, zero-threshold lasing, lossless guiding of light, dispersion management, and nonlinear frequency conversion. Future prospects include applications in telecommunication, optical signal processing, and transistors. In addition, with this type of technology, there is the possibility of creating high efficiency optoelectronic devices such as waveguides with sharp bends and low-threshold lasers [10].

But the fabrication of photonic crystals with a full 3D band gap in the visible range is still a challenging task, mainly limited by the resolution and flexibility of already available technologies. For practical applications of photonic crystals, inexpensive and reliable nanofabrication techniques are required. The most promising technique for the fabrication of photonic crystals is two-photon polymerization [11]. The ability of 2PP to create complex 3D structures with exceptionally high resolution makes this technology advantageous for the fabrication of 3D photonic crystals. With this technique, one is able to introduce defects at any desired location, which is crucial for the practical applications of photonic crystals [12]. Few groups employing 2PP have reported the fabrication of photonic crystals exhibiting photonic band gap effects. One of the first papers, which marked the important achievement that revealed great potential of 2PP for the fabrication of photonic crystals, employed a frequency doubled femtosecond laser radiation at 400 nm to write a woodpile structure, shown in Figure 1-3, which consisted of 20 layers in the Nopcocure 800 resin.

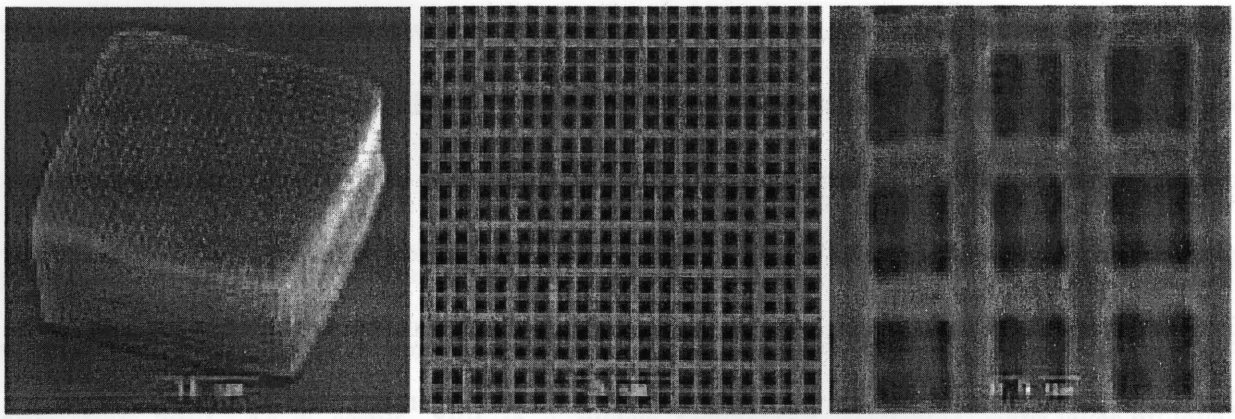


Figure 1-3: Woodpile structures fabricated by means of 2PP using Ormocer photoresist taken by SEM [13]

Although the fabrication aspect remains a challenging task, there are at least two advantages to fabricating PhCs using two-photon photo polymerization technology. First of all is the potential to produce PhCs of arbitrarily designed lattices. PhCs of varied lattice types, lattice constant, and filling factors are realizable just by scanning different CAD patterns. This simplicity in fabrication permits a systematic study of PhC physics and suits various requirements for a practical system. Secondly, there is the diversity of usable materials and functions. The progress of molecular material engineering has made it possible to synthesize polymers with performances similar to or better than their inorganic counterparts. By introducing functional groups to unsaturated monomer or oligomer units in a molecular structure, or just by doping the functional polymers into known photopolymerizable materials, optical, electronic, magnetic, and mechanical functions can be imparted to devices [14].

Holographic recording is a method that allows fast fabrication of large 3D crystals with long range periodicity and up to few millimeters in dimension. The idea is to record an interference pattern created by two or more beams into a photosensitive material. If the beam parameters are chosen properly, it is possible to polymerize photosensitive resins at the high

intensity regions while leaving the rest of material non-polymerized. This can be achieved if light intensities at the interference maxima are larger than the threshold value for polymerization and intensities at the minima are lower than the polymerization threshold. Tuning the intensity inside this working window changes the filling factor and therefore, has an effect on stability of the structure. The material that is not polymerized is then washed out to reveal a solid 3D mesh in air [15-18].

1.5.2 BIOMEDICAL APPLICATIONS

There are several very promising biomedical applications of the 2PP technique such as: tissue engineering, drug delivery, medical implants, and sensors. When dealing with tissue engineering, the ability to produce arbitrary 3D scaffolds is very appealing. Artificial fabrication of living tissue that will be able to integrate with the host tissue inside the body is a challenging task. Natural repair of a tissue at the particular site is a result of complex biological mechanisms which are the subject of intensive research [19]. In order to encourage cells to build such a tissue, one has to create an appropriate environment exactly resembling that of a particular tissue type. Some cell types can preserve tissue-specific features in a 2D environment, others require a 3D environment. Another problem that becomes critical with increasing scaffold size is possibility of blood-vessel formation throughout the scaffold, in order to promote healing and to avoid hypoxia. 2PP in combination with the right materials allows the precise control over 3D geometry of the scaffold, and therefore, allows to model and to reproduce the cellular microenvironment. Furthermore, high resolution of 2PP can provide control over the cell organization inside the scaffold and consequently over the cell interactions. Another advantage of 2PP is that near-infrared laser radiation, used for 2PP, is not dangerous for cells at the applied

intensities and could also be used for the manipulation and encapsulation of cells [19]. Microneedle arrays for drug delivery were fabricated using two photon induced polymerization. Using 2PP, one can produce microneedles with a large range of sizes, shapes, and improved properties. Microneedles provide a unique approach for transdermal drug delivery of DNA- and protein-based pharmacologic agents Two photon induced polymerization is able to create microneedles with a larger range of sizes, shapes and materials than conventional stainless steel or titanium micro fabrication techniques. An Ormocer microneedle array was created on a glass substrate using two photon induced polymerization. These hollow microneedles demonstrate much larger wall thicknesses than those observed in microneedles created using conventional micro fabrication techniques. Future studies will involve use of two photon induced polymerization to fabricate microneedle arrays with even greater microneedle densities and larger microneedle wall thicknesses [20, 21].

1.5.3 MICROMECHANICAL AND MICROFLUIDIC DEVICES

Further promising applications of two-photon activated (2PA) processing are in the field of rapid prototyping and fabrication of micromechanical and microfluidic systems. Since the resolution limit of 2PP is at present about 100 nm, it is possible to build gearwheels with a diameter of around 1 μm. Because 2PP is the real 3D processing technology, any desired structure can be built. As a result, both single elements for micromechanical systems and complex constructions can be produced by this specific technique [22].

The other possible field of applications is microfluidics. Using 2PA technique, it is possible to build 3D microfluidic and optical devices on the same type of chip. A good example of such implementation is the ring resonator microcavity. The cavity is fabricated in positive

photoresist and is surrounded by four mirrors, which are aligned ninety degrees to with respect to each other. The emitted light from a dye solution inside the cavity can be directed around the resonator by total internal reflection. A horizontal cut is made through the device and the dye can be injected via microchannels. The device itself, which also can be fabricated completely, is buried in the resist. This technique provides a simple method for the fabrication of different imbedded microstructures and microfluidic devices [23, 24].

1.6 RESEARCH OBJECTIVES

The main intention of this thesis is to characterize and enhance the knowledge about two-photon polymerization technique as a general 3D fabrication process. That means that all the parameters that influence this technique have to be engaged in depth. As of now, various applications in different fields of scope of the 2PP technique indicate that this process has blossomed over the past decade and achieved rapid success. But none the less, there is always room for improvement in certain areas such as: further increasing the spatial resolution and widening the range of applicable materials.

Using femotsecond lasers to produce features that are so small in size that they are simply imminent to make an impact in various industries has created a high demand and interest in this nanofabrication technique. As a result of this potential impact, the following are explored in the scope of this thesis:

- Study the distinctive capabilities and advantages proposed by femtosecond lasers on 2PP technique.
- Study the fundamentals of 2PP and its applications for the purpose of influencing current market demands.

In chapter 5, the effect of pulse width and laser power on aspect ratio is reported. These parameters were then used to produce the highest aspect ratio possible with the given equipment. Additionally, it has been determined that the choice of substrate plays an important role in achieving the given task. Ultimately, the curve pattern that aspect ratio produces was analyzed and as a result, it has been observed that the highest aspect ratio structure was formed at 214 fs pulse width and by using silicon substrate material

In chapter 6, the results obtained from this research work are summarized. In addition, the achievements and the limitations of the proposed 2PP technique using femtosecond laser system are discussed. Further research suggestions that can be employed are mentioned as well.

- Optimize certain laser parameters such as repetition rate, pulse width, scanning speed, laser power, and exposure time and evaluate the influence of these parameters on quality and size of the features produced.
- Evaluate the influence of pulse width, laser power, and scanning speed on aspect ratio of the polymerized features.

1.7 OVERVIEW OF THESIS

In chapter 2, general principles of 2PP are discussed in details. Available materials for processing and two photon absorption, which is the standard acting origin of 2PP, are summarized with special attention paid to resolution.

Details of the experimental setup are presented in chapter 3. The overall positioning and the sequence of the lenses and the mirrors that the laser beam passes through are described. In addition, the general polymerization principle, through which the feature size is created and shaped, is iterated.

The important laser parameters that play a role on the polymerized feature size produced are identified and discussed in chapter 4. Crucial parameters such as repetition rate and laser were found to affect feature size in an important manner. It was observed that the combination of lower laser pulse energies and higher repetition rates leads to lower size of the polymerized feature. Furthermore, silicon substrate was proved to be the better material when coated with SU-8 photoresist due to its good edge and pattern visibility as well as minimal surface disruption. However, Ormocer photoresist demonstrated overall dominance by producing the smallest feature size qualities that are contributed mainly to its chain of three dimensional networks of organic-inorganic polymers, which in result lead to outstanding optical and mechanical properties.

CHAPTER 2

TWO-PHOTON POLYMERIZATION

2.1 INTRODUCTION

The possibility of very high localization of laser energy has led to more and more advanced laser applications. Particularly, the interaction of lasers with polymers and dielectrics is of high technological interest. The main issue is placed in the adjustment of polymers to laser characteristics which can be very challenging process from the scientific and technological points of view. Two-photon polymerization of photosensitive materials irradiated by femtosecond laser pulses is now considered as an enabling technology for the fabrication of 3D structures using photosensitive materials. This micro structuring technology provides a much better structural resolution and quality than the commonly used stereo-lithography (SL) techniques. Despite the fact that two-photon polymerization technique is considered to be a very young technology in comparison and has only been around a decade or so, it nonetheless, impacted many fields, such as photonic crystals and photonic crystal templates, in a significant matter. 2PP technique has also been used in biomedical applications and micromechanical and microfluidic devices.

2.2 TWO-PHOTON ABSORPTION

For the past decade, the process of two photon absorption (TPA) has taken an enormous step into the future progress of microfabrication. It was not until 1961 with the invention of the laser, which supplied the high intensities required, that an experimental demonstration of TPA took place [25]. High power is the absolute requirement that has to be met in order to achieve a

sufficient value of intensity squared, which in result coerces TPA to occur. Furthermore, since two-photon polymerization is proportional to the square of the light intensity, for it to be observed, a laser is needed to provide the high intensity factor. A continuous-wave laser that was available at the time did not have such capabilities and for that reason, TPA did not find broad use for many years after its demonstration and was used only for selected applications [26]. This situation changed drastically in the late 1980s and early 1990s with the development of relatively simple, solid-state femtosecond laser [25]. Overall, TPA is a matter radiation interaction process in which an atom is excited from a lower quantum state to a higher state in a single step. This process, which is of a third order and is optically non-linear, is implemented without any excited intermediate state with the two photons playing a critical role by interacting with a medium. Since the two photons have to be absorbed simultaneously, high intensities are needed for the process to occur. As a result, the molecule maintains the energy difference between the two photons. This process is also known for its penetration capabilities by being able to record deep in surfaces. However, a potential setback exists in its short length of coherence which can be avoided by generating transient high power commonly present in picosecond lasers, which have coherence lengths in the order of millimeters.

Multi-photon absorption uses ultrafast pulses for the purpose of maskless micro fabrication techniques. These ultrafast pulses are produced by Ti:sapphire laser, which has numerous advantages attributed to its domineering presence in the manufacturing industry. A typical Ti:sapphire laser puts out pulses with a duration of 100 fs at a repetition rate of approximately 80 MHz. As a result, the time between pulses is therefore on the order of 12 ns. In addition, low average laser power has a sufficient enough peak intensity to create efficient photon absorption. While the output of a Ti:sapphire laser is in the range of hundreds of

milliwatts, two-photon excitation can generally be accomplished at average powers of a few mW or less, depending on the focusing conditions and the specimen being excited. It is important to mention that two-photon absorption is an essential tool in laser spectroscopy since transitions between two states that cannot be connected by dipole transitions can be observed. In general, two-photon absorption is a fundamental process fabrication technique that makes two-photon polymerization possible [25].

2.3 MATERIALS

Polymers are usually the materials that are chosen for the purpose of micro-fabrication in 2PP technique. The main reason for being in such popular demand is due to their ease of processing and fabrication as well as being very inexpensive. Flexibility is also a well known factor of polymer materials in which they are modified into composites to achieve a better chemical and physical functionality.

The best example of a polymer material from a structural point of view is Ormocer, which is set of organic-inorganic hybrid polymer combinations. These set of polymer materials are produced from liquid precursors using sol-gel process, where inorganic-oxidic units are connected to organic molecules such as urethane, and contain strong covalent bonds between the inorganic and organic components [19, 27]. The cross-linking of inorganic and organic molecules leads to the formation of a 3D network, which provides Ormocer with significant chemical and thermal stability as well as tremendous flexibility by variation of the catalysts, temperature, and alkoxysilane scaffold [28]. These hybrid polymeric materials are characterized by a relative high malleability and a low shrinkage coefficient (<2%) [29]. In addition, the refractive index of Ormocer materials is located in the 1.47–1.56 range [30]. The fact that

photonic applications are more promising due to the material's high transparency in the visible spectral range and high refractive index is a well known fact that is established in Ormocer's material properties. The combination of Ormocer with 2PP technique enables the creation of any computer designed structures. Furthermore, during the sol-gel synthesis, the ratio between the organic and inorganic network density can be changed, offering a possibility to generate Ormocer materials with desired mechanical, optical, chemical, and surface properties [31]. The specific elasticity can be altered as well and as a result, the generated structures can be adapted to different shapes and movements [32]. Since its material properties can be tailored precisely during synthesis, Ormocer is suitable for a wide range of applications in dielectric and optical microelectronics. Ormocer materials have recently received increased interest from the medical device community. Biological examinations have shown that Ormocer materials are nontoxic and biologically inert. In addition, Ormocers-based matrix components and Ormocers-based light-curable dental composites have been used in restorative dentistry since 1988 [20].

Ormocer is an example of a commercialized photoresist that can form microstructures by a single-step curing procedure upon exposure to light. Other photoresists that share the similar feature pattern include: SCR500 from Japan Synthetic Rubber Company, Nopcocure 800 from San Nopco, Japan, and NOA63 from Norland Products Inc [8, 33]. All these photoresists are polymerized through a single-step radical initiated process and contain a PI which cleavages to produce radicals during light exposure. The polymerized resin is confined to the focal spot of a light beam, while the whole fabrication process can be monitored and optimized with adjusting the fabrication parameters. Although polymerization is a single-step procedure, the light treatment of a sample can be various according to the different requirement of fabrication. Photoresist, such as Nopcocure 800, is pre-exposed to UV light to increase its viscosity. As a

result, the resin is completely solidified by a 2PP process. For rapid fabrication of bulk structures, only the contours have to be irradiated by femtosecond laser pulses. After washing away the non-irradiated, liquid resin, the structure can be exposed to UV light resulting in solidification of the inner volume. A bulk structure can also be formed through layer-by-layer laser scanning procedure as a standard 3D sterolithography process

Photoresists used to fabricate micro-structures are multi-functional monomers or oligomers. A PI (photo initiator) is chosen to be added into the photoresist through solvent-mixing process. A pulsed laser beam excites the initiator to produce radicals or cations. As a result, they interact with the surrounding monomers to trigger a polymerization chain reaction as shown in 1PP and 2PP reactions. Multi-functional monomers can form a cross linked network within the focal volume of the laser beam, which cannot be dissolved by any solvent. The photoresist is solidified by the two-photon excitation beam through the pre-programmed light pathway to form a 3D micro-structure. The non-cross linked monomers maintain good solubility in certain solvents and can be washed away after the 2PP process, leaving a 3D micro-structure which is an exact replicate to the pathway of the laser focus. After polymerization, the refractive index generally changes to a slightly higher value, which increases the contrast in refractive indices between the polymer and air. This behavior enhances the performance of photonic crystal structures.

The development step usually involves washing the sample in a solvent or a series of solvents. There are two types of photosensitive materials; positive photoresist and negative photoresist. When a positive photoresist is used, the exposed region is softened due to the creation of shorter units, which are eventually washed away by the developer. Negative photoresist operates in the exact opposite manner in which the non-illuminated area is removed

by the developer and the exposed region is hardened due to cross-linking of polymer chains [21]. This particular fact can be seen in Figure 2-1:

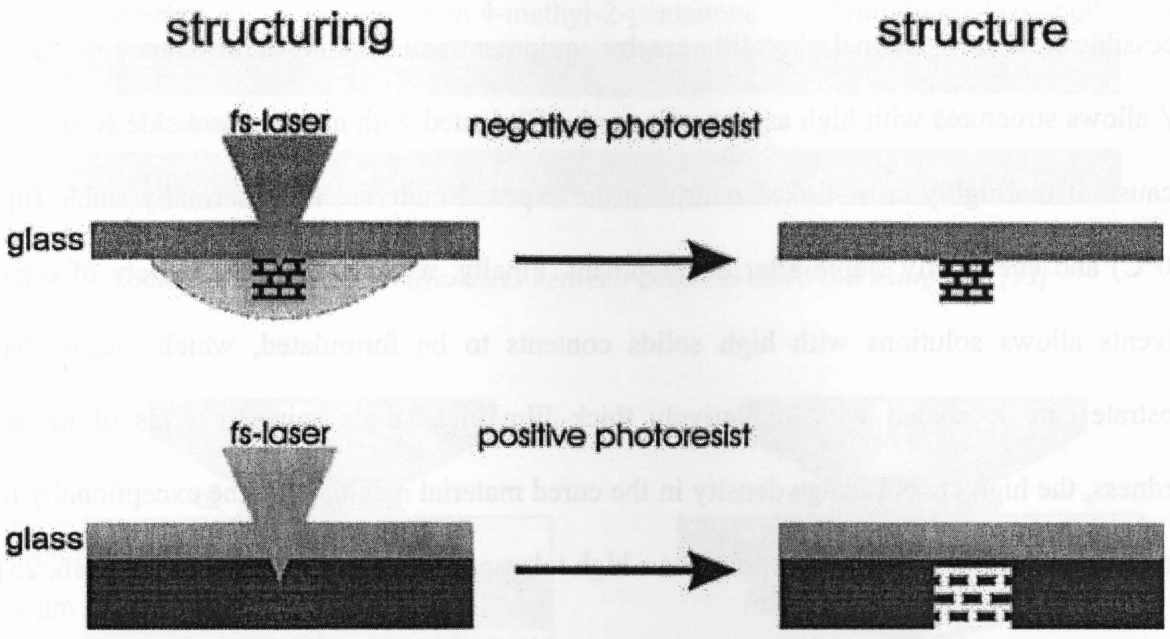


Figure 2-1: Difference between negative photoresists (top) and positive photoresists (bottom) [6]

Furthermore, photosensitivity of positive photoresist is much higher than that of Ormocer or SU-8. Taking into account that structures in positive photoresists can be easily removed by solvents, these two properties make them very attractive for the fabrication of templates and three-dimensional replicas.

A number of resins have been used for micro-fabrication, some of which have been commercialized. SU-8 is provided by MicroChem which is originally developed for the microelectronic industry. Regarding to the chemical process, only resin SU-8 has a two-step cross linking procedure. The resist has several attributes which make it suitable for micromachining applications and microstructure fabrication. First, there is the formation of a

strong acid during the exposure process within the focal spots, followed by an acid-initiated, thermally driven epoxy cross linking during the post-exposure bake step. The product is supplied as a liquid consisting of an epoxy resin a solvent and a photo-acid generator. Then, there is the photosensitivity of SU-8 which is measured to be between 300-400 nm [34, 35]. This region is accessible with conventional photolithography equipment and the high transparency in the near UV allows structures with high aspect ratios to be fabricated with near-vertical side walls. Also, because of the highly cross-linked matrix in the exposed material, it is thermally stable (up to 200°C) and chemically stable after development. Finally, its solubility in a variety of organic solvents allows solutions with high solids contents to be formulated, which means that a substrate can be coated with a relatively thick film in a single spin. In terms of radiation hardness, the high cross-linkage density in the cured material results from the exceptionally high epoxy functionality which in turn provides a high tolerance to absorbed radiation dose [36, 25].

The main differences of those two classes of materials are as follows: First, during exposure, Ormocers are in the liquid phase whereas SU-8 is solid. Second, Ormocers are thermally very stable whereas SU-8 can be removed by calcinations. Third, online monitoring of the 2PP process is only possible in Ormocers since crosslinking in SU-8 does not occur before the application of heat (up to this moment there is no refractive index modification in SU-8). The fact that Ormocers are liquid and SU-8 is solid also leads to different exposure strategies and sample configurations as shown in Figure 2-2. The steps needed for the fabrication of 3D microstructures by means of 2PP using Ormocer and SU-8 materials are summarized in Table 2-1.

Procedure	Ormocer	SU-8
Soft Bake	1 min at 80 °C	50 min at 95 °C
Exposure	fs pulses P = 45 mW	fs pulses P = 20 mW
Post Bake	No	12min at 95◦C
Develop	30s in 4-methyl-2-pentanone	15min in mr-Dev.-600
Rinse	Isopropanol	Isopropanol
UV Curing	Yes	No
During Exposure	Liquid Phase	Solid Phase

Table 2-1: Fabrication differences between Ormocer and SU-8 using 2PP [13]

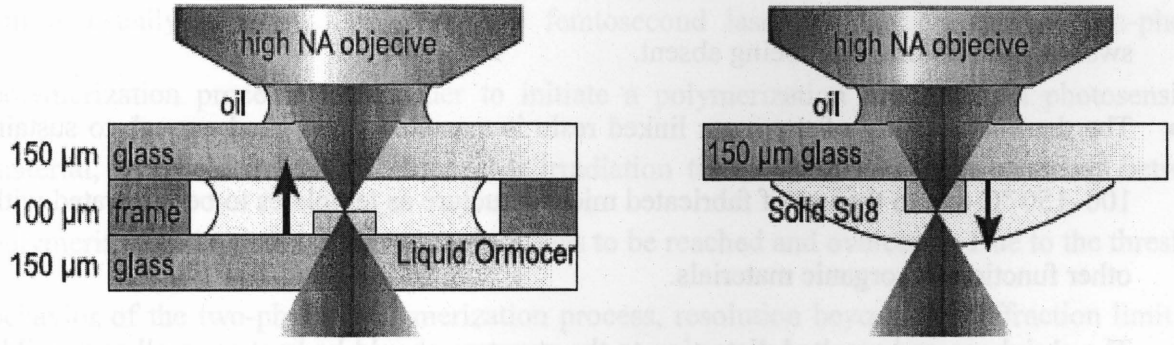


Figure 2-2: Different sample configurations indicating the phase of the polymer [13]

Although commercial photoresists have good performance, the composition of photoresists is uncertain and unchangeable. Due to the reason that some fabricated optical devices have special requirements such as high resolution, high curing speed, good thermal stability, and transparency at certain wavelengths, customer-made resins are also developed in research laboratories. Customer-made resins have certain benefits. One of the advantages of such a resin is that it can be formulated with specific components to adjust the mechanical and surface properties of the resin and different initiators can be chosen to be adapted to the laser wavelength. As a result, the

concentration of an initiator can be optimized to obtain the best structure, and more efficient initiators can be applied to resin systems [7].

In general, photoresists that are involved in the fabrication process must have the following properties [7]:

- Little or no scattering should be present with polymerized area confined to the focal spot.
- Transparent in the visible and near infrared region to allow for focusing the laser pulses into the volume of the resin without any single-photon interaction.
- Fabricated micro-structure remains unharmed upon the development process with swelling and deformation being absent.
- The thermal stability of the cross linked resin is expected to be good enough to sustain 100–150 °C due to the use of fabricated micro-structure as templates to be infiltrated with other functional inorganic materials.
- The shrinkage and resulted distortion to the structure should be kept as small as possible during polymerization process.
- The material should be flexible and tough enough to sustain the deformation of shrinkage while at the same time being hard enough to maintain the structure shape.
- Fast curing speed.
- The highly cross linked material should have washout resistance to be able to withstand high developer currents.
- Refractive index of the resin before fabrication should be close to that of glass (approximately 1.5) for the ability of the beam to be focused deeply into the resin without aberrations to access a large vertical dimension.

2.4 RESOLUTION

The resolution of two-photon polymerization process is limited by several factors that are identical to a single photon polymerization process due to the similarities between the two methods. Resolution quality is basically limited by factors such as laser and material characteristics, material composition, and the order of process nonlinearity with the addition of the well-known resolution limit of photolithography.

The first limit is exhibited in material and laser characteristics in which the resolution is restricted by the proximity that 2PA threshold can be approached. A wavelength of around 780 nm is usually used by the Ti:sapphire femtosecond laser for the purpose of two-photon polymerization processing. In order to initiate a polymerization process in a photosensitive material, threshold irradiation fluence or irradiation time, which acts as a boundary between polymerized and non polymerized regions, has to be reached and overcome. Due to the threshold behavior of the two-photon polymerization process, resolution beyond the diffraction limit can be realized by controlling laser pulse energy and the number of applied pulses [37]. More specifically, for this to occur, the laser powers have to be just slightly above the threshold limit, as can be seen in Figure 2-3. In order to predict the size of the polymerized volume, a polymerization threshold has to be defined. Under the assumption that the resin is polymerized as soon as the specific amount of initiator molecules is activated and the particle density of radicals, $\rho = \rho(r, z, t)$, exceeds a certain minimum concentration, ρ_{thres}, which acts as a threshold value. Due to the rotational symmetry of the intensity distribution, ρ can be treated as a function of z (distance to the focal plane in cylindrical coordinates) and r (distance to the optical axis in cylindrical coordinates), and here t is the total processing irradiation time. For the same initiator,

ρ_{thres} is independent of the particular initiation process that leads to the generation of radicals and should be the same for both single and TPA [7].

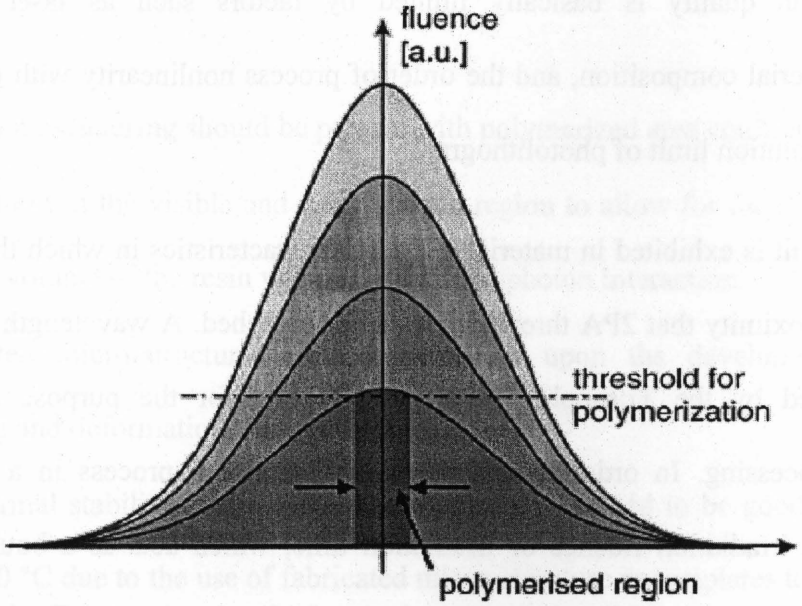


Figure 2-3: Light intensity distribution model due polymerization threshold in the laser focus [6]

The other limit is material composition, which refers to the properties of the photosensitive matter that is used in the course of the exposure. In Ormocer (organically modified ceramic; ORMOCER®s, Trademark of the Fraunhofer-Gesellschaft zur Forderung der Angewandten Forschung e.V., Munich, Germany) for example, the smallest structure is limited by the size of the individual organic and inorganic unit that ranges between 2 and 10 nm.

The last factor affecting multi photon polymerization resolution limit is determined by the order of process nonlinearity, linear or multiphoton processing. The classical resolution limit is set by the laser wavelength and by the numerical aperture (NA) of the imaging optics. The resolution limit of photolithography is defined by the following equations [6]:

$$CD = \frac{k_1 \lambda}{NA}$$

Eq. 2-1

$$DOF = \frac{k_2 \lambda}{NA^2}$$

Eq. 2-2

Eq. 2-1 and Eq. 2-2 can be then rewritten into the following equations:

$$CD = \frac{k_1 \lambda}{\sqrt{q} NA}$$

Eq. 2-3

$$DOF = \frac{k_2 n \lambda}{\sqrt{q} NA^2}$$

Eq. 2-4

Where CD is the critical dimension of the printed structure size, DOF is the depth of focus, q is the order of the multi photon process which is equal to two in 2PP process, λ is the exposure wavelength, NA is the numerical aperture of the objective ($NA = r / f$ where r is the radius of the lens and f is the focal length), and k_1 and k_2 are factors whose quantity is dependent on the illumination technique, photoresist material, and process technology. The immersion oil refractive index in an ordinary used high numerical aperture immersion oil microscope objective is abbreviated as n. This limit corresponds with the resolution limit of photolithography in which the equations are modified to fit the multi photon polymerization model.

In general, to achieve the best resolution possible, it is important to work at low laser energy and short irradiation time, i.e. close to the polymerization threshold. This gives not only the best resolution, but also the best (closest to spherical) shape of the polymerized voxel.

2.5 INFLUENCE OF INITIATORS

In the photo polymerization technique, upon light excitation, the monomers and oligomers, which are the basic components of the starting liquid material, may be solidified by two methods: polymerization and cross linking. An important difference between these two reactions lies in their quantum yield, which is defined as the ratio of number of polymerized monomer units to the number of photons that are needed to cause this polymerization to occur. While cross-linking is more concerned with the formation of cross links through chemical bonds, polymerization is more focused on the macromolecules that are formed through chain reaction. In the case of photo cross linking, addition of each monomer unit requires absorption of a photon, leading to a quantum yield less than 1. In contrast, photo polymerization is realized via chain reactions as shown in the following equation and the value of the quantum yield can reach several thousand [5]:

$$M \xrightarrow{M} M_2 \xrightarrow{M} M_3 \cdots M_{n-1} \xrightarrow{M} M_n \qquad \textit{Eq. 2-5}$$

Where M is the monomer or oligomer unit and M_n is the macromolecule containing n monomer units.

In reality, this system is much more complicated due to the addition of certain components such as photo initiators. Since the quantum yield of monomers and oligomers is generally low, an increase in efficiency is necessary. In order to accomplice such a task, one or several low-weight molecules that are more sensitive to light irradiation are added. The photo initiators molecules are called as such due to the formation of initiating species of free radicals or

reactive cations by absorbing photons that attack monomers and oligomers. The small PI particles are part of the photo initiation process, which is the most important step in the 2PP process.

Upon exposure to the UV light or two-photon of NIR light, the photo initiator is dissociated by light to produce free radicals via molecular bond cleavage. The bond must have dissociation energy lower than the excitation energy of the reactive excited state. After absorbing energy from UV light or two-photon of NIR light, an initiator transfers from ground state to excited singlet or triplet state. Part of the absorbed energy may be lost due to internal conversion from excited state to ground state and some reactive intermediates can be quenched by oxygen, another monomer or a combination of intermediates. Monomer quenching is usually an indication of inefficient energy or electron transfer. The polymerization rate depends on the light source intensity, the photon initiator concentration, the presence of oxygen and additives, the quantum yield of the radical generation, and the initiation efficiency of generated radicals. Generally, the rate is increased with the incident light intensity but not with initiator concentration. If an initiator has high extinction coefficient, high concentration of initiators can lead to inefficient energy transfer. Different concentrations of initiators can also lead to different molecular weight and molecular weight distributions resulting in final polymer with various mechanical properties. Therefore, the concentrations of initiators should be chosen carefully to obtain the optimized performance of a micro-structure [8, 38].

The polymerization process consists of several different steps: photo initiation, followed by chain propagation, and finally termination [19, 39].

$$I \xrightarrow{h\nu} I^* \longrightarrow R\cdot$$

Eq. 2-6

Where I is a photo initiator, R· is a radical and I* is an intermediate state of the photo initiator after absorbing a photon.

Eq 2-5 can be further summarized and the polymerization process is more precisely described by the chain propagation that is described by the following equation:

$$R\cdot + M \longrightarrow RM\cdot \xrightarrow{M} RMM\cdot \cdots \longrightarrow RM_n \qquad \textit{Eq. 2-7}$$

Eq. 2-7 indicates how the photo produced radicals react with monomers or oligomers and as result, generate monomer radicals, which in turn combine with new monomers. Through similar effect, the monomer radicals continue to expand in a chain reaction until two radicals meet with each other.

This chain propagation will eventually reach the termination stage and will come to a halt in either of the following cases:

$$RM_n\cdot + RM_m\cdot \longrightarrow RM_{m+n}R \qquad \textit{Eq. 2-8}$$

$$RM_n\cdot + RM_m\cdot \longrightarrow RM_n + RM_m \qquad \textit{Eq. 2-9}$$

From the breakdown of photo initiator reactions, it can be clearly understood that an ideal photo intiator should have high molar absorption coefficients, a low extinction efficient and a well-adapted spectral absorption range. Furthermore, it should be easily reduced to an initiating species upon light irradiation in addition to being able to produce intermediate with excellent

reactivity and photolysis by-products with low toxicity. Finally, it should Further it should be compatible with monomer and oligomers, dispersing in the monomer uniformly before photon polymerization [5].

When referring to 2PP initiator, one major difference has to be mentioned. Since in 2PP process, an initiator absorbs two NIR photons with a long wavelength through non-linear absorption, two NIR photons are absorbed simultaneously by a PI molecule. The difference between one photon and two photon induced photo polymerization lies in how the energy for activating initiators is provided. Since in 2PP initiators are excited to triplet states by absorbing the combined two-photon energy, Eq. 2-4 should be rewritten as following:

$$I \xrightarrow{2\,h\nu'} I^* \longrightarrow R\cdot \qquad \textit{Eq. 2-10}$$

The molecules in normal UV initiators should have a two-photon absorption cross-section as well as high efficiency to produce reactive intermediate radicals or cations, which can proficiently activate the chemical functionality. The same principles are applied to a two-photon initiator. As a result of using two-photon initiator with high initiation efficiency, the photo-sensitivity of whole system is increased. Due to this fact, the polymerization threshold is lowered and the polymerization rate is increased and as a result, the laser writing window can become broader and the possibility to damage the structure due to the high fabrication intensity can be drastically reduced. In addition, the long exposure time associated with commercial UV initiators is reduced and the spatial resolution is further increased, which is a key factor in 3D fabrication [8, 40].

2.6 SUMMARY

In summary, 2PP is a rapid three-dimensional technique that uses ultra short laser pulses induced to produce nanoscaled particles. The main focus point of this technique revolves around resolution and its ability to produce the smallest feature size possible. There are several factors, such as laser and material characteristics, material composition, and the order of process nonlinearity, that determine the resolution limits of 3D multi photon material treatment with femtosecond lasers. Nonetheless, the nonlinear threshold character of two-photon micro structuring processes allows the fabrication of structures in all cases with a resolution in the sub wavelength range.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 INTRODUCTION

Selection of laser system and understanding of the laser parameters are most essential for the laser 2PP process operation. In this chapter, an overview of the laser system selected for this study is provided and the experimental setup is discussed. These experiments were conducted using a high power high repetition rate femtosecond laser in the Micro and Nano Fabrication research lab at Ryerson University, Toronto, Canada.

3.2 EXPERIMENTAL SETUP

All experiments were done by using Clark-MXR IMPULSE™, an all-diode-pumped, direct-diode-pumped Yb-doped fiber oscillator/amplifier system capable of producing repetition rates ranging from 200 KHz to 25 MHz. Average output power is 20 W at repetition rate of 2 MHz. The Yb-doped fiber-oscillator/fiber-amplifier operates under low noise performance associated with solid state operation with the addition of high spatial mode quality of fiber lasers. Furthermore, the parameters of the laser, such as: repetition rate, pulse width and total beam power are controlled by a computer that allows a simple interaction with the performed experiments. The pulse width ranges between 250 fs and 10 ps. The central wavelength of the laser beam is measured to be around 1030 nm.

The system is set in such a way that the laser beam is expanded through a plano-convex lens of 500 mm focal length and a plano-concave lens of 150 mm focal length. A λ/2 wave-plate placed between the two optical lenses is used to rotate the polarization of the beam. A harmonic generator is employed to convert the beam to the second harmonic (515 nm) central wavelength. Shorter wavelength has been proven to increase the efficiency of micromachining due to multiphoton absorption [41]. In addition, the purity of the laser beam is further increased by the removal of 1030 nm wavelength by three consecutive series of mirrors with reflective coating at 515 nm. Furthermore, a plano-concave lens of 75 mm focal length and a plano-convex lens of 300 mm focal length are utilized to increase the beam diameter to 8 mm. A quarter wave-plate that ensures circular polarity of the beam is located between the two optical lenses. Next, the beam steered to scan across the sample surface using a uniquely designed piezo tip/tilt mirror. The mirror consists of two fixed orthogonal axes with a common pivot point [42]. Field distortion or the pillow effect is a common problem faced with galvoscanners. Normally, correction software is needed to compensate for the distortion. With a common pivot point, field distortion can be completely eliminated. The mirror itself evades any friction and stiction and has a high resonant frequency of 1 KHz [22]. Such high frequency is of great importance to high repetition rate laser machining since precise pulse number control demands for high frequency beam steering. Finally, the laser beam passes through a telecentric lens with a 12.478 mm focal length and is focused onto the sample surface [43]. The theoretical laser machining spot diameter, D_0, was calculated from the following equation [44]:

$$D_0 \approx 1.27\frac{\lambda_0 f}{D} \qquad \textit{Eq. 3-1}$$

Where, f is the effective focal length of the telecentric lens equal to 12.478 mm, λ_0 is the wavelength of the laser equal to 515 nm and D is the laser beam diameter equal to 8 mm. From this formula the theoretical spot size is calculated to be 1.02 μm in diameter.

A piezo-scanner is used for high speed laser beam positioning and the samples are mounted on a two-axis (x and y) translation stage with a precision step of 0.5 μm. Substrates of silicon, glass, and gold thin film that was deposited on a silicon substrate were used as samples.

It is important to mention that two negative photoresists have been used in this study. Although both SU-8 and an Ormocer photoresists share a similarity by being transparent in the visible and the near infra red ranges, they composed of variety of microstructures and hence made a difference in feature size performance. Ormocer is a chain of a three dimensional network of organic-inorganic polymers that contain strong covalent bonds between the ceramic and polymer components and as a result lead to an outstanding optical and mechanical quality as well as thermal and chemical stability. In addition, the networks contribute to exceptional properties of the Ormecer by preventing it from splitting into separate phases [7]. On the other hand, SU-8 is not very stable from a thermal prospective since the photoresist itself can be removed by calcinations at a normal atmosphere of 600°C. But the main difference between the photoresist polymers remains the exposure circumstances where SU-8 is at a solid state and the Ormocer is at a liquid state [1]. Furthermore, the fact that the two photoresists are vary in their exposure states means that the exposure procedures and approaches will eventually lead to Ormocer prevailing by accomplishing a smaller feature size than its fellow SU-8 photoresist counterpart. By observing the refractive index of both photoresist materials in which Ormocer's value ranges between 1.48 and 1.59, and SU-8 value has been reported to be close to 1.65, it is correct to assume that additional factors are responsible for the formation of a small feature size

[7]. However, there is a major obstacle that has to be overcome when using photosensitive resins in general (positive or negative). This problem lies in the distortions that are created within the structures and caused by the shrinking upon cross linking processes. This can be solved either by producing a thick frame surrounding the structure or by numerical compensation [7].

As discussed in detail in chapter 4 and chapter 5, the laser beam has been scanned at different velocities with a repetition rate of 13 MHz and 26 MHz with pulse width of 214.29 fs to 3.5 ps. Generally, samples are prepared on a substrate to which the photoresist adheres well. As a result, the structures that are fabricated contact the substrate over a large enough area to not be washed away upon development. Immediately after the substrate is coated, it is then heated up during the prebaking process in order to make sure that the coating is properly adhered to the surface. The substrate is then exposed to the laser irradiation. Desired image of the potential structure is directly imprinted by the laser on the photosensitive material and the substrate is then post baked for 5 minutes. The post baking is done to improve the adhesion of the thin film to the substrate. After that, the developer solution washes out the unexposed regions and leaves the polymerized material intact [13]. The sample evaluation was carried out under a scanning electron microscope (SEM). To increase the conductivity of the polymer structures, samples are gold sputtered before imaging by SEM. Figure 3-1 shows the laser apparatus that was involved and Figure 3-2 shows the schematic drawing of the experimental setup.

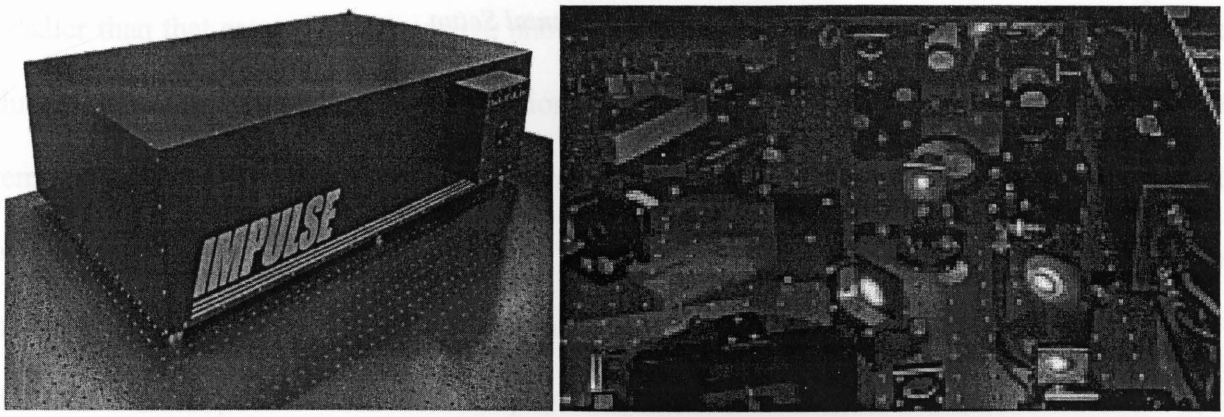


Figure 3-1: Laser Apparatus

1. 1030 nm Mirror
2. F = 500 mm Convex Lens
3. 1030 nm λ/2 Waveplate
4. F= -150 mm Concave Lens
5. 515 nm Harmonic Generator
6. 515 nm Mirror
7. 515 nm Mirror
8. F= -75 mm Concave Lens
9. 515 nm λ/4 Waveplate
10. F = 300 mm Convex Lens
11. 515 nm Mirror
12. Diaphragm
13. Piezo Scanner
14. EFL = 12.478 mm Telecentric Lens

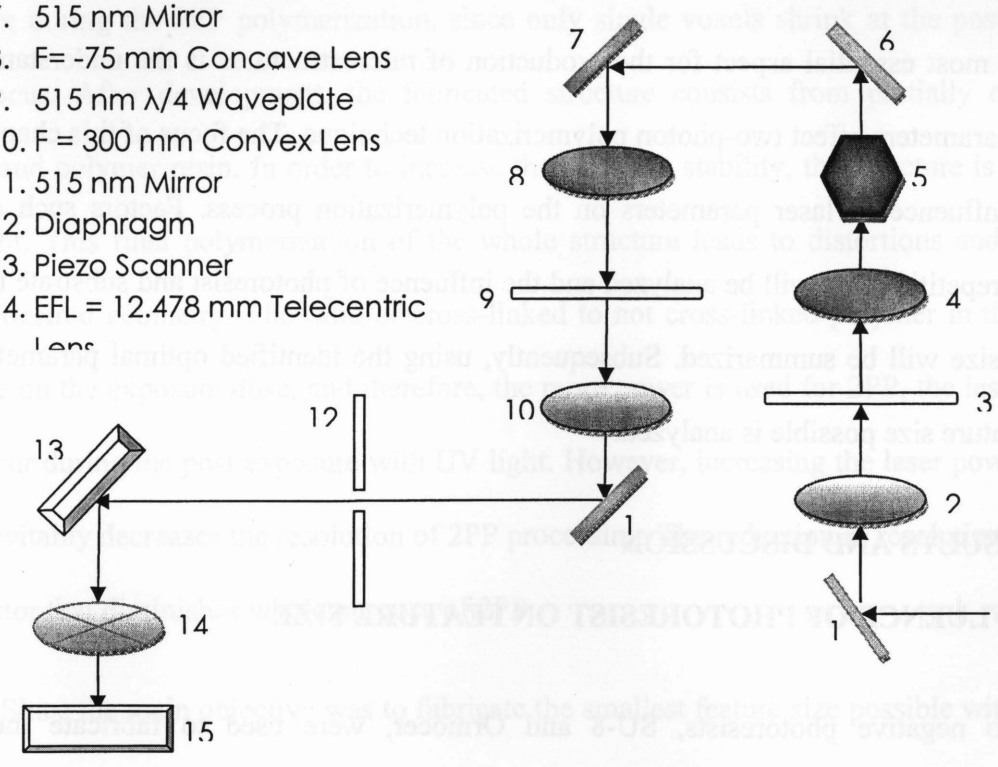


Figure 3-2: Experimental Setup

CHAPTER 4

EFFECT OF LASER PARAMETERS ON TWO-PHOTON POLYMERIZATION

4.1 INTRODUCTION

The most essential aspect for the production of microstructures is the understanding of how laser parameters affect two-photon polymerization technique. The focus of this chapter is to study the influence of laser parameters on the polymerization process. Factors such as laser power and repetition rate will be analyzed and the influence of photoresist and substrate material on feature size will be summarized. Subsequently, using the identified optimal parameters, the smallest feature size possible is analyzed.

4.2 RESULTS AND DISCUSSION

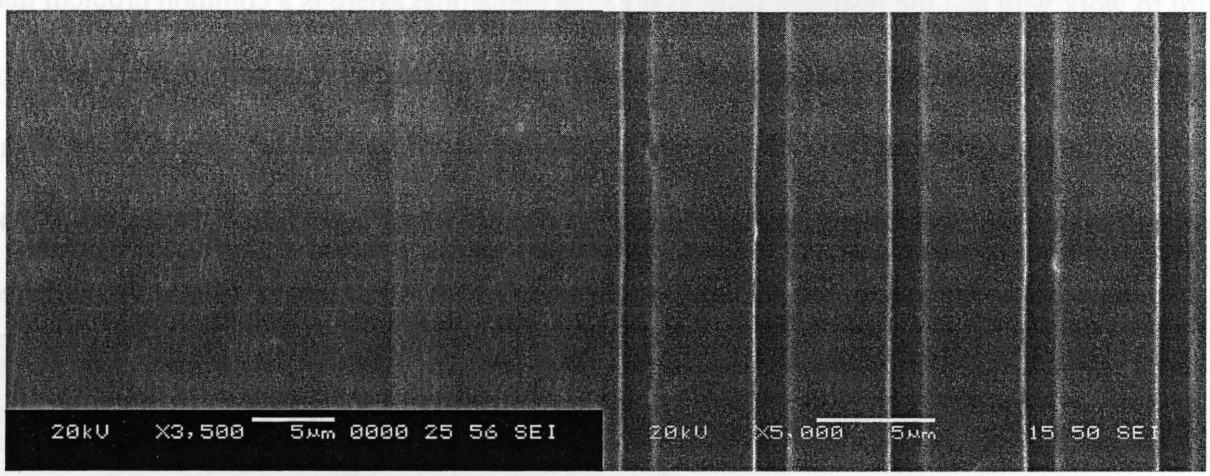
4.2.1 INFLUENCE OF PHOTORESIST ON FEATURE SIZE

Two negative photoresists, SU-8 and Ormocer, were used to fabricate the three-dimensional features on the substrate. However, the two main advantages of using a positive photoresist over a negative one is that with positive photoresist the resolution is four times

smaller than that created with negative photoresist and positive resist has the ability to produce three dimensional templates [8]. Application of most negative photoresists for the fabrication of templates is rather complicated, since the structures fabricated in these materials are quite stable and not simply soluble. In case of positive photoresist, the polymer is weakened and is usually more soluble in developing solutions, which is very attractive for the fabrication of three-dimensional templates. Furthermore, photoresist-substrate-adhesion is much stronger with positive photoresist. As far as 2PP is concerned, the main reason for choosing to work with negative photoresists in the beginning comes about from the fact that positive photoresists are hard to work with and the resulting features are quite appalling. There is a common problem that exists with the processing of negative tone photosensitive polymers, which lies in the shrinkage of the produced structure. However, In the case of Ormocer, shrinkage does not affect the structure during the 2PP polymerization, since only single voxels shrink at the position of the laser focus. After development, the fabricated structure consists from partially cross-linked voxels and polymer resin. In order to increase the structure stability, the structure is exposed to UV light. This final polymerization of the whole structure leads to distortions and deviations from a desired geometry. The ratio of cross-linked to not cross-linked polymer in the structure depends on the exposure dose, and therefore, the more power is used for 2PP, the less shrinkage will occur during the post exposure with UV light. However, increasing the laser power used for 2PP inevitably decreases the resolution of 2PP processing. The reduction in resolution can in fact be a factor that diminishes whole purpose of 2PP.

Since the main objective was to fabricate the smallest feature size possible with the given laser parameters, an initial concept of having a thin layer of photoresist material seems viable. But due to aspect ratio inconsistencies and laser machining characteristics, this concept becomes

implausible. Given the fact that polymerization occurs initially at the subsurface level between the substrate and the photoresist and then develops further through the photosensitive material, a thicker resist layer will definitely produce a smaller feature size as the thick layer of photoresist acts as an immersion lens (air to film) and thus focusing the beam to a greater extent [11]. For this reason, a relatively thick layer of photoresist coating will enable the production small feature sizes in nano scale, as seen in Figure 4-1. While thin coating layer, on the other hand, will further prevent the laser beam from significant refraction and thus thwart it from bending and proper focus.



(a) (b)

Figure 4-1: Sample of a polymerized feature on glass substrate material of
(a) Ormocer at 0.08 W and 26 MHz repetition rate
(b) SU-8 photoresist at 0.250 W and 26 MHz repetition rate

Ormocer photoresist coating was applied at a thickness of 25 µm and the resulting line width was measured to be around 410 nm. In contrast, as can be seen in Figure 4-1, SU-8 photoresist was applied at a coating thickness of 0.5 µm and as a result, the line width became reasonably thicker and was measured accordingly to be 4.51 µm.

4.2.2 INFLUENCE OF SUBSTRATE MATERIAL ON FEATURE SIZE

The material of the substrate plays a very important role in the production of nano-structures using two-photon polymerization technique in terms of image visibility, pattern linearity, and light reflectivity. Every substrate material exhibits different reflectivity patterns to laser light. The more light is reflected, the less the chances become for the structure to be properly adhered to the surface of the substrate. There is also a possibility that the nano-structure will be fully or partially washed away as soon as the developer is applied. Using the technology of two-photon polymerization, only a certain amount of materials can be worked upon.

The three materials that were analyzed for this study were silicon, glass, and gold thin film. The gold thin film of 3000 Å silicon substrate thickness is deposited on top of a silicon substrate. Each of the substrate materials were coated with two different photoresists (SU-8 and Ormocer). Silicon substrate material exhibited the most remarkable results when coated with SU-8 photoresist by having straight lines and clear edges as can be seen in Figure 4-2.

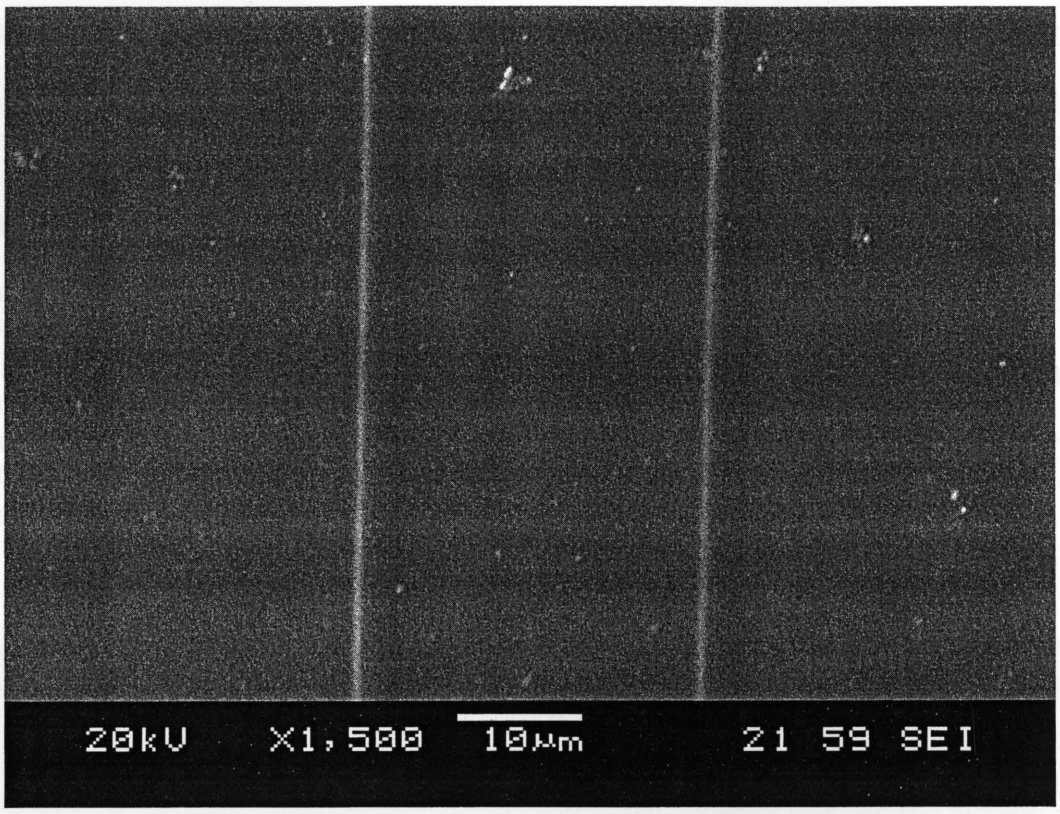


Figure 4-2: Polymerized feature produced on the silicon substrate material by the SU-8 photoresist

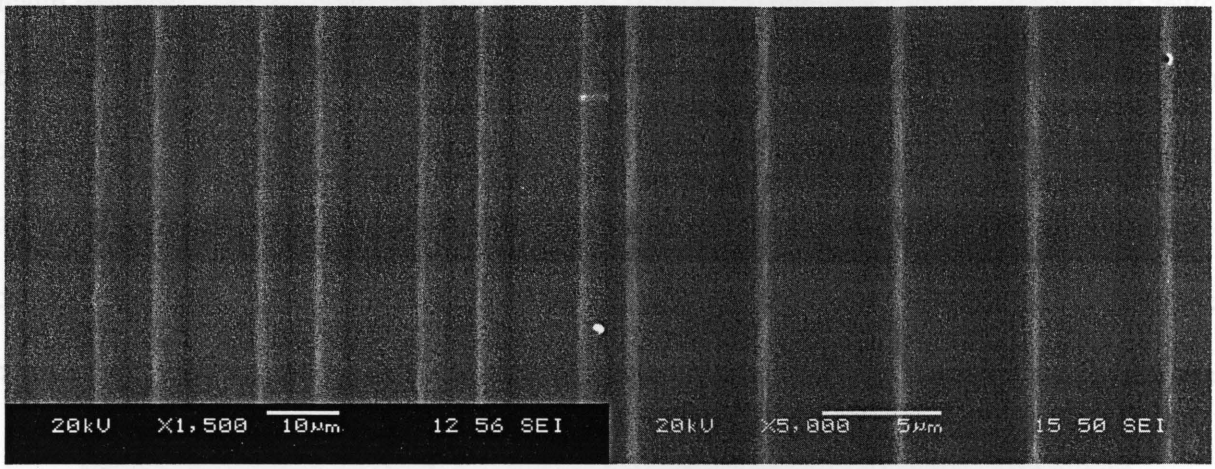
The sample shows relatively no surface disruption as well as good edge and pattern visibility. In addition, particles that scattered around the structural lines in the figure, as well as in several figures below, are the result of gold sputtering.

The reflectivity of glass substrate was measured as 92%, while that of a silicon substrate is around 30%. Gold coated silicon substrate showed reflectivity of about 34%. Due to the energy lost in the transmitted light, the polymerization threshold energy, which is the amount of energy needed to start two-photon absorption and polymerization, is the highest in glass and the lowest in silicon. As a result of adhesion problems, glass substrate material demonstrated fluctuated results that at times were in the acceptable range, as at the repetition rate of 26 MHZ, and at different times were completely distorted, as in repetition rate of 4 MHZ. Due to this fact, farther experiments were carried out under repetition rates of 13 and 26 MHZ only.

Overall, glass substrate material displayed better quality than gold coated substrate material but performed poorly due to substrate adherence and pattern distribution when compared to a silicon substrate. Figure 4-3 (a) shows SU-8 photoresist been applied to a glass substrate material and the resulting feature, whose line width is 4.63 μm, is produced at repetition rate of 8 MHZ, power of 0.065 W, and at a speed of 2500 μm/s. Figure 4-3 (b), on the other hand, shows a much smaller feature size, whose line width is measured to be 460 nm, that is produced at a repetition rate of 26 MHZ, power of 0.207 W, and at a speed of 10,000 μm/s. Although both features are prepared from the same photoresist inscribed in glass substrate material, the images of the two feature sizes are quite different. This is due to the different laser parameters imposed on the two samples. In general, lower pulse energy at a high repetition rate gives better machining resolution since debris is produced at lower scale and heat affected zone is sharply reduced.

The substrate material that was coated with gold, on the other hand, showed the poorest results among the three different surfaces in terms of boundary visibility as well as surface disruption. This fact can be seen in Figure 4-4 and 4-5, as edge fluctuations and surface disturbances are most likely due to the lack of light absorption and light reflectivity of the given surface [45]. Figure 4-4 demonstrates the feature size, whose line width was measured to be 4.09 μm that is formed once SU-8 photoresist is applied to a thin film of gold at repetition rate of 26 MHZ, power of 0.133 W and at a writing speed of 5000 μm/s. Overall, the gold coated substrate material sample shows that shows unacceptable results in terms of continuity and pattern clearness. The feature size in Figure 4-5, whose line width was measured to be 2.11 μm, is produced at repetition rate of 13 MHZ, power of 0.204 W and at a writing speed of 10000 μm/s. This gold coated sample, similar to the previous figure, shows poor pattern distribution and poor surface adherence. The same particles, which were visible in Figure 4-4, can be also seen in

Figure 4-5 and can act as markers that mark the initial size of the structure. As a result, it is clear that the thermal treatment that is done during prebaking of the substrate results in an increased refractive index of the material, and simultaneously decreased structural size [2]. However, in order to obtain non-distorted structures, more control over the material shrinkage is necessary.



(a) (b)

Figure 4-3: Polymerized features produced by the laser on the glass substrate material by SU-8 photoresist

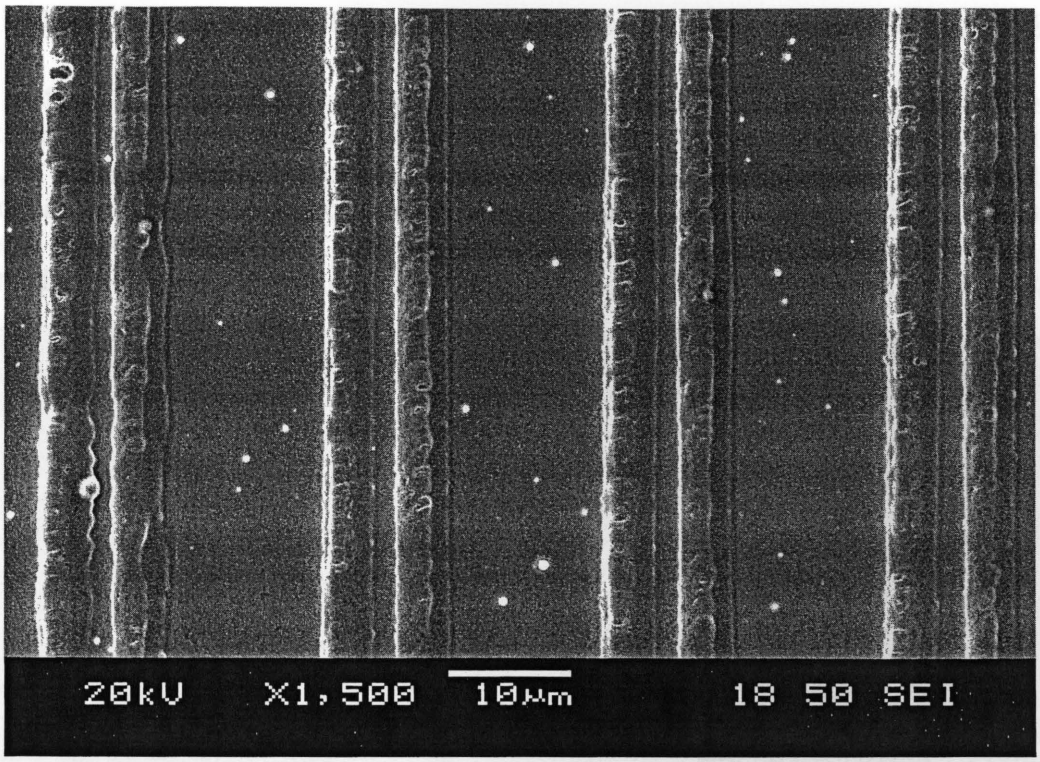


Figure 4-4: A polymerized pattern of SU-8 photoresist on the gold coated substrate material

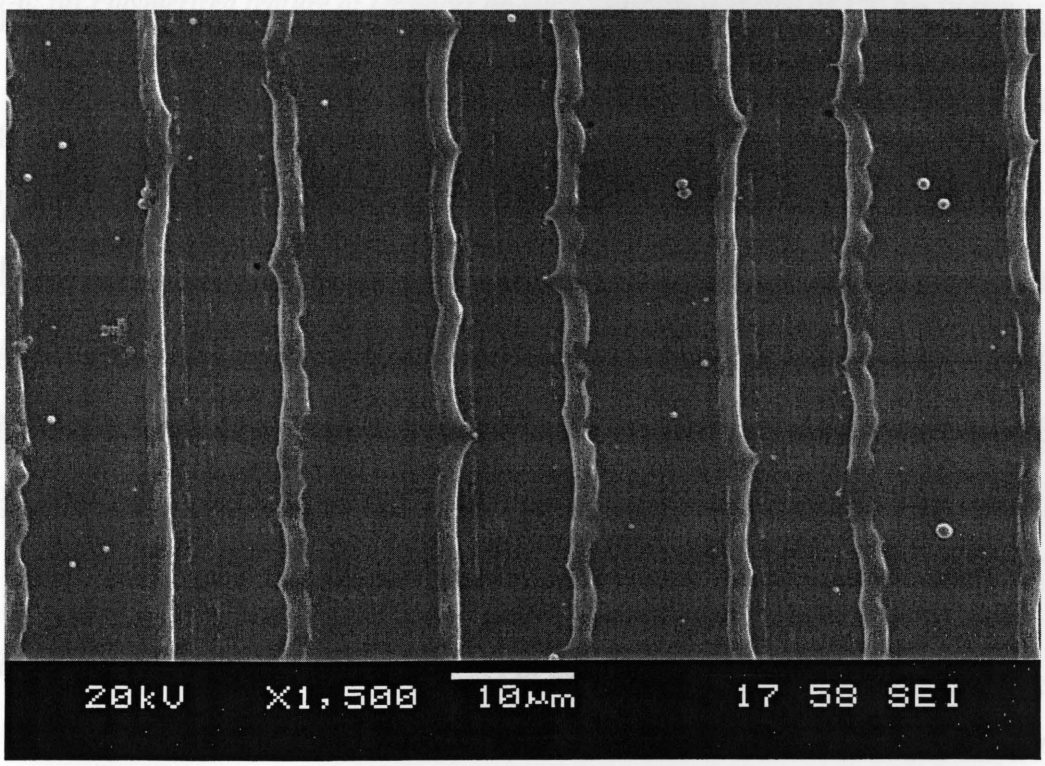


Figure 4-5: Polymerized feature produced by the laser on the gold substrate material by the SU-8 photoresist

4.2.3 EFFECT OF LASER POWER AND REPETITION RATE ON FEATURE SIZE

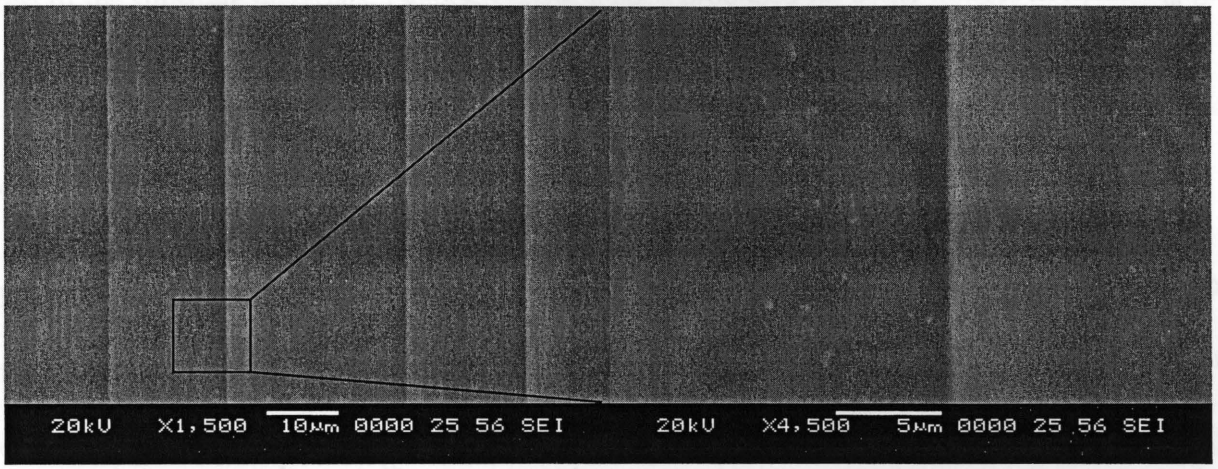
In principle, there are two different illumination techniques that are used for the fabrication of structures using two-photon polymerization: continuous scanning and pinpoint illumination [46]. Continuous scanning technique, whose resolution is changed by adjusting the scanning speed and the average laser power, has been used throughout all the experiments and the presented data in this report.

The influence of laser power and repetition rate on feature size was studied. In order to accomplish such an objective, a multiple scan of each line with a gradually increasing average laser power is necessary. The average laser power was slowly increased from 5 mW with increments of 15 mW until up to a point that no further polymerization occurred and where laser ablation of the supporting substrate has been initiated. It was found that a slower scanning speed had to be implemented in order to produce a well-defined homogeneous structure. Each line was scanned with velocities of 4000 and 10000 μm/s.

Every substrate that is coated with a certain photosensitive material has a power range in which polymerization occurs in a precise manner that reduces feature size dramatically. Any power above or below the necessary optimal limit will produce indistinct patterns mainly in terms of the polymerization process. An example of such an optimal range was observed in Figure 4-6, where Ormocer was coated on glass substrate material at 0.07 W and at a repetition rate of 13 MHz.

Feature size and laser power is plotted in Figure 4-7 and 4-8 at speeds of 4000 and 10000 μm/s, respectively. In general, it can be concluded from the chart in Figure 4-8, that as the laser power continues to increase at a constant repetition rate, the feature size also increases. In

addition, each repetition rate is distinctive in pattern with higher repetition rates demonstrating smaller feature sizes when compared to lower energy repetition rates at the same power level. As a result, in order to create features in nanometer scale, higher repetition rates (13, 26 MHz) are preferred.



(a) (b)

Figure 4-6: (a) Polymerized feature of Ormocer on glass substrate material of 350 nm in size (b) Enlarged section of the image shown in the figure

From comparison of Figures 4-7 and 4-8, it can be concluded that in both cases, the minimum feature size is around 2 μm. It can also be concluded that the feature size increases with the increase of the repetition rate. Furthermore, the rate of increasing is relatively high at lower repetition rate. On the other hand, the rate of increase is at a minimum at 10000 μm/s scanning speed and at 26 MHz repetition rate. This is an indication of the controllability of the feature size through laser power. Hence, in order to properly be able to control the feature size through laser power, repetition rate of 26 MHz should be used. In addition, Figure 4-7 also indicates that polymerization threshold power is higher at higher repetition rates.

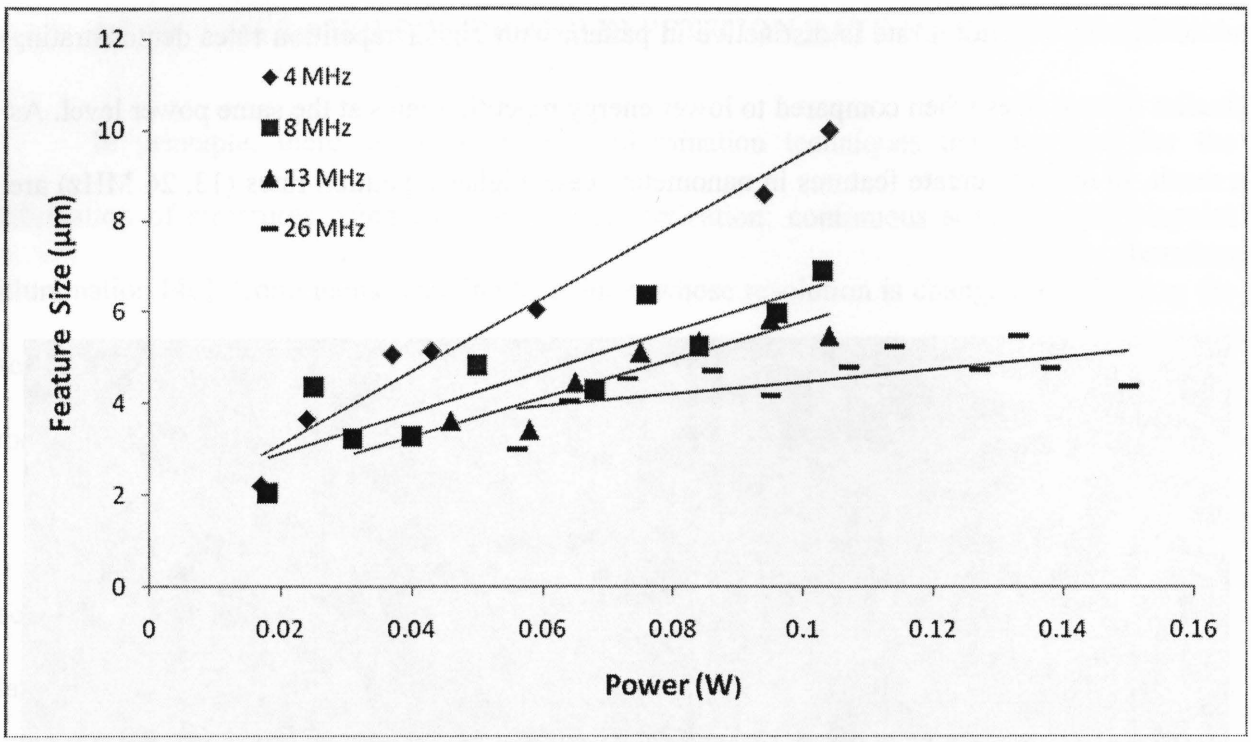


Figure 4-7: The relationship between feature size and power under different repetition rates on a silicon substrate material at a speed of 4000 µm/s

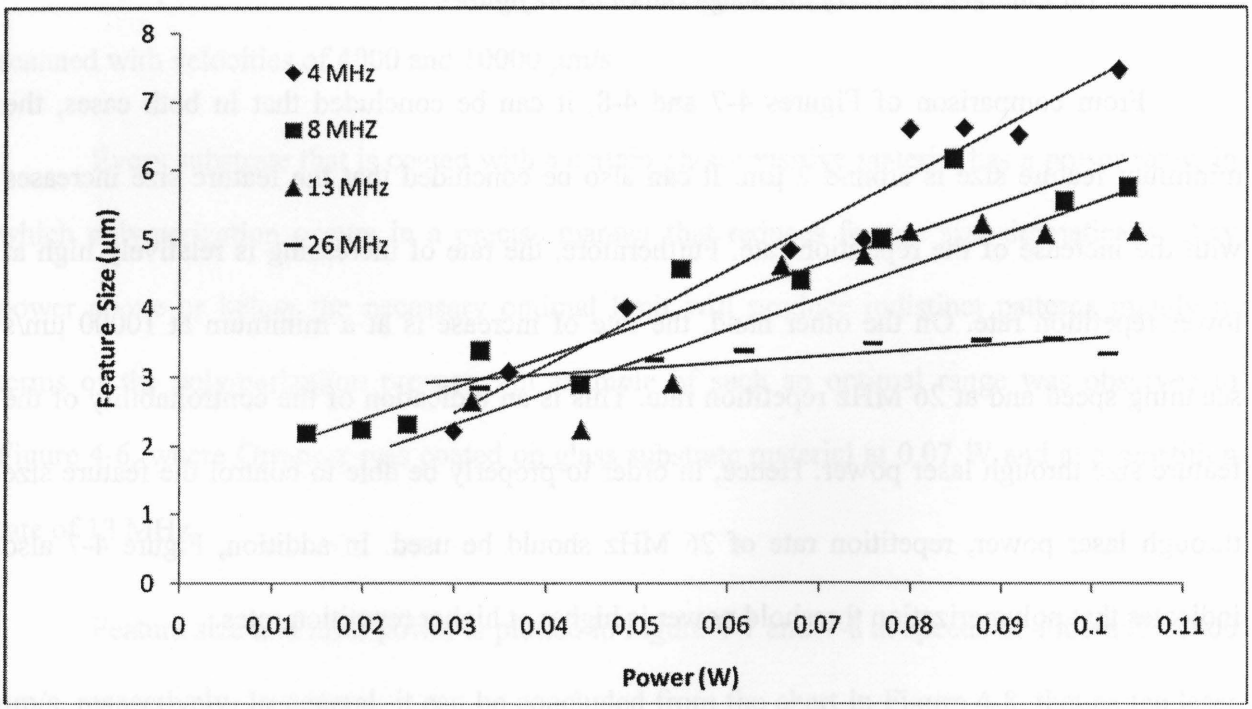


Figure 4-8: The relationship between feature size and power under different repetition rates on a silicon substrate material at a speed of 10000 µm/s

Based on the experiments and on the previous images, it is possible to conclude that a slow writing speed, low pulse energy, and multiple exposures are needed in order to obtain well-defined lines. In addition, at higher repetition rates, silicon substrate showed better light absorption qualities and structure characteristics. This pattern also holds true in the case of the rest of the substrate materials. Higher repetition rates produced far better images in terms of light reflectivity, picture visibility and pattern continuation.

4.3 SUMMARY

Recent progress in three-dimensional micro structuring of photosensitive materials by femtosecond lasers using two-photon polymerization technique has been outstanding. Many current applications have been revolutionized by this very powerful technology and although various innovative approaches have been taken place, some areas still remain an uncertainty. One of these areas has always been the feature size phenomenon, in which the requirement to strive to the production of a minimal feature size is mandatory. The parameters that were introduced in this chapter, such as repetition rate and laser power, influence the production of a feature size that is as small as possible. In addition, fabrication of three-dimensional patterns was done by Ormocer and SU-8 photoresists on different material substrates such as silicon, glass, and gold thin film. It can be concluded that the combination of high repetition rate and low laser power become of high importance in producing the smallest feature size possible with the silicon substrate and the Ormocer photoresist playing a critical role. Two-photon polymerization technique is still in its rapidly developing phase and represents a very exciting tool for the future of micro fabrication technology.

CHAPTER 5

ASPECT RATIO

5.1 INTRODUCTION

2PP process has been the gemstone byproduct of the rapid developing and ground-breaking nanotechnology. Each and every three dimensional polymerized feature produced by such technique has a fabricating resolution composed of a block-like layer method. Although lateral spatial resolution is a relatively distributed matter, aspect ratio has not been touched upon in detail. Furthermore, there are several factors of great importance and have a major influence on aspect ratio growth that have not been neither discussed nor thoroughly studied. The focus of this research is to study the influence of laser power, laser pulse width, and substrate material on aspect ratio. Subsequently, using the identified parameters, the feature with the highest aspect ratio will be analyzed. Additionally, the predisposition of the pulse width will be studied and its effects on 2PP process will be investigated.

A silicon substrate with an Ormocer photoresist coating, which was applied at a thickness of 25 μm, was used as a sample for this experiment for the purpose of studying the factors that influence aspect ratio. For the purpose of studying the influence of a substrate on aspect ratio growth, glass substrate material was coated with Ormocer photosensitive material. All the experimental data was conducted at a repetition rate of 26 MHz. An experimental analysis was successfully performed on pulse width ranging from 214 fs to 714 fs. In addition, all the experimental values that were taken at each pulse width were obtained with three different scan speeds of 2500, 5000, and 10000 μm/s.

5.2 CONTROL OF ASPECT RATIO

Aspect ratio, although independent of spatial lateral resolution, is an important factor in 3-D micro-fabrication. High aspect ratio features demonstrate the superior controllability of laser parameters and the advanced knowledge and usability of the general laser system. But nonetheless, producing features at a nanoscopic scale and maintaining a high aspect ratio pattern can be a tremendously difficult task to accomplish. The reason lies in two-photon absorption photo-polymerization technique, where a microstructure with high aspect ratio can be deformed or distorted during the rinsing process [47]. After the polymerization stage is complete and the polymerized features stay undamaged and fully intact, an image, such as in Figure 5-1, should be evident.

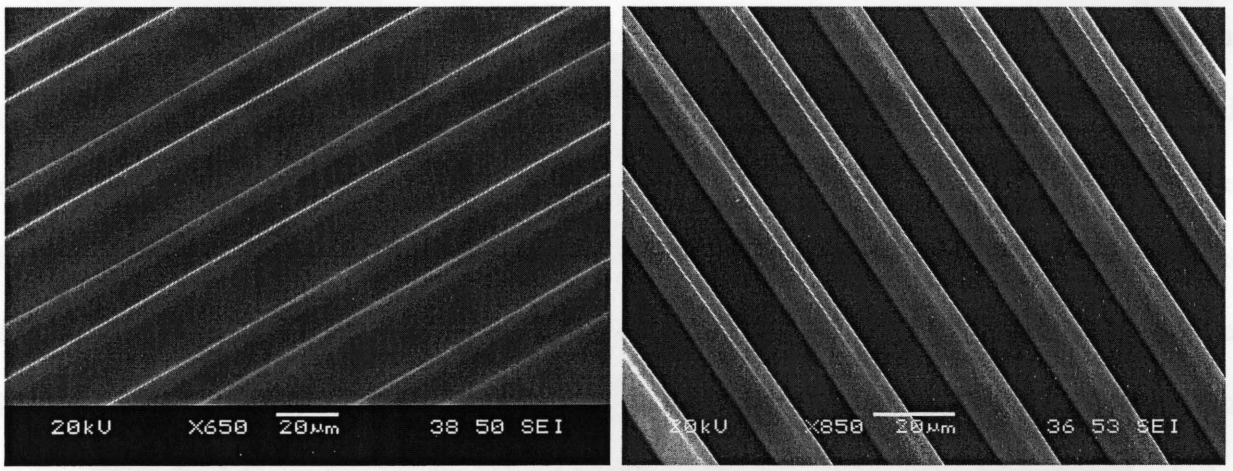


Figure 5-1: A set of polymerized microstructures on silicon substrate material

The relationship between aspect ratio and the critical factors that affect it such as laser power and pulse width is a popular phenomenon that has been studied although not yet explained. In order to achieve such an undertaking, a multiple scan of each line becomes a necessity. A gradually increasing average laser power with increments of 20 mW from a

polymerization threshold of around 55 mW up to a point where no further polymerization occurs is necessary to identify and locate the exact point where the value of aspect ratio is the maximum. Furthermore, a progressive decrease of the laser power from an ablation point to the starting polymerization process position is done in order to achieve more accurate results and the verification of previous measurements.

Based on the experiments and on the previous figures, it is possible to conclude that the highest aspect ratio achieved in this research paper by implementing the controllability of pulse width, laser power, and silicon substrate material was around 7.37, as shown in Figure 5-2. Previously, the highest aspect ratio achieved was 6. As a result, tremendous effort in controlling laser parameters has been done in order to be able to achieve such a task. Another polymerized structure having high aspect ratio is evident in Figure 5-3.

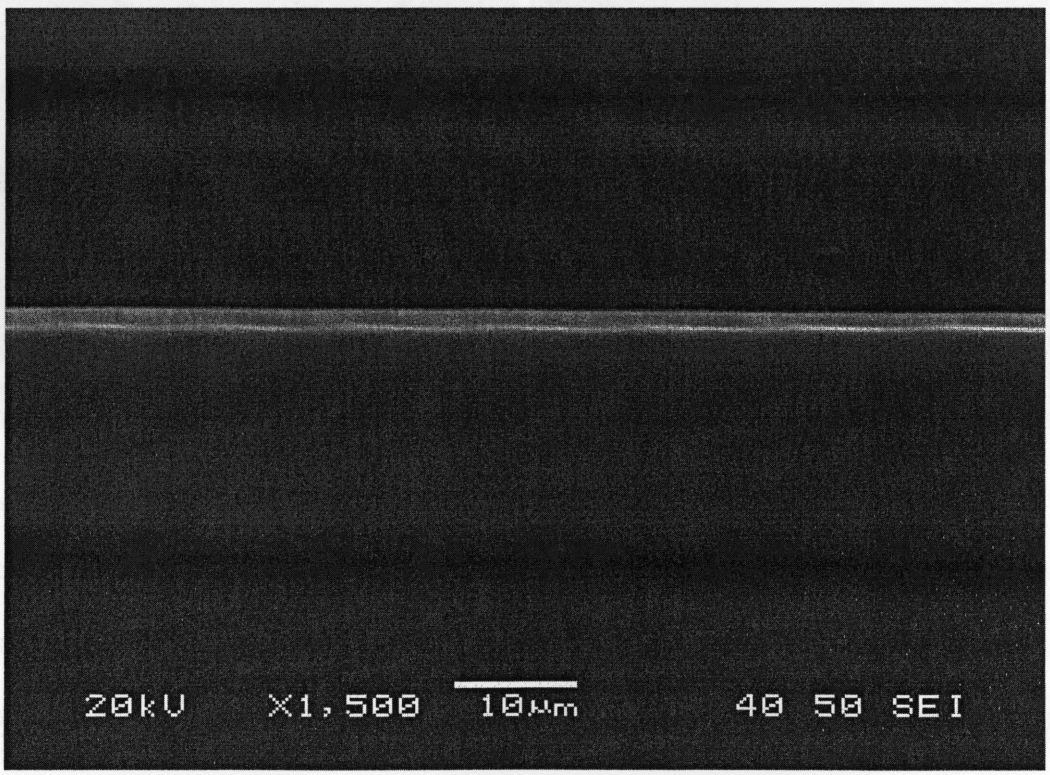


Figure 5-2: Polymerized feature on a silicon substrate having a high aspect ratio of 7.37 at 0.104 W laser power, 214 fs pulse width, and 5000 µm/s scanning speed

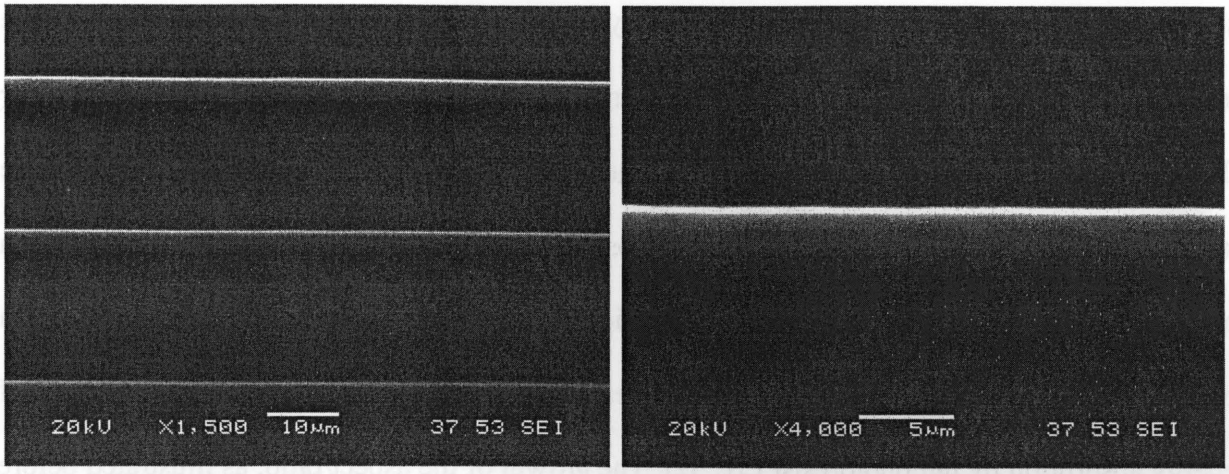


Figure 5-3: Polymerized feature having a relatively high aspect ratio of 4.7 at 0.104 W laser power, 214 fs pulse width, and 10000 µm/s scanning speed

5.3 RESULTS AND DISCUSSION

5.3.1 EFFECT OF LASER POWER ON ASPECT RATIO

Aspect ratio analysis from the affiliation between measured parameters such as laser power has been studied. Previous research, theoretical calculations showed that the lateral spatial resolution can be increased dramatically with reduced laser power. Specifically decreasing the laser power to less than 0.8 mW can significantly improve lateral spatial resolution [48]. This fact also holds true in the case of the relationship of laser power and aspect ratio, as can be seen in Figure 5-4, where reducing the power of the laser produces an overall increase in aspect ratio at a constant speed of 2500 µm/s. Based on laser investigation purposes and precision analysis, laser power is represented as laser fluence.

Several interesting key points are demonstrated in Figure 5-4. The shape of the curve, for example, indicates a fascinating occurrence that shows great resemblance to the distribution model of the polymerization threshold process. Initially, aspect ratio increases with increasing laser fluence, at which point, a maximum value or a peak is achieved. From that point on, there is

a decreasing non-linear pattern that eventually stabilizes as the value of the laser fluence increases. The explanation lies in the nonlinear resin absorption process [49, 50]. As laser fluence is increased, the aspect ratio grows higher due to the increased energy absorption of the laser energy to the phototresist material. The absorption of laser light occurs through excitation of the outer atomic electrons and energy deposition into the material by this nonlinear absorption process. Correspondingly, aspect ratio is decreased due to energy relaxation and the lack of energy absorption by the photoresist [51, 52]. The growth of the aspect ratio, as illustrated before in Figure 5-4, can be shown schematically in Figure 5-5, where the maximum peak value is determined by photoresist composition as well as laser characteristics. Higher aspect ratio can be produced by using different photosensitive materials whose smallest structure is limited by the size of the individual microstructures that exhibit lower nanoscopic scales [6].

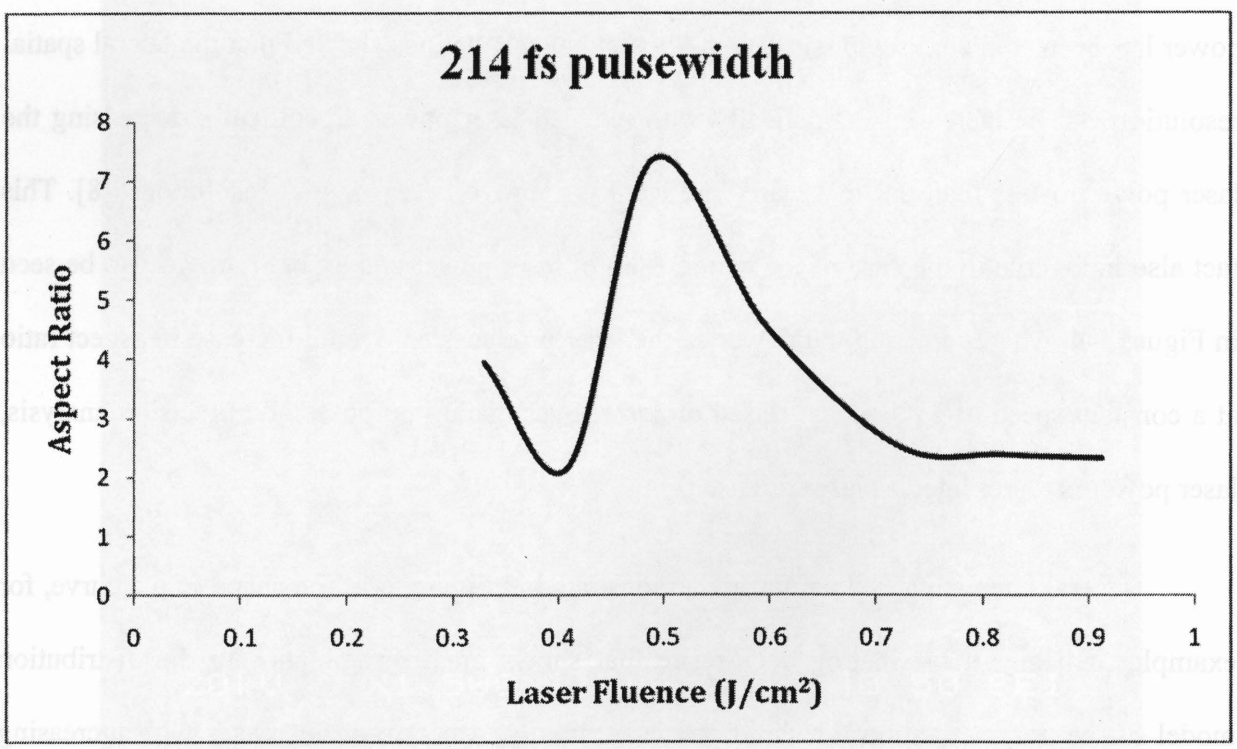


Figure 5-4: The relationship between aspect ratio and laser fluence at a speed of 2500 μm/s

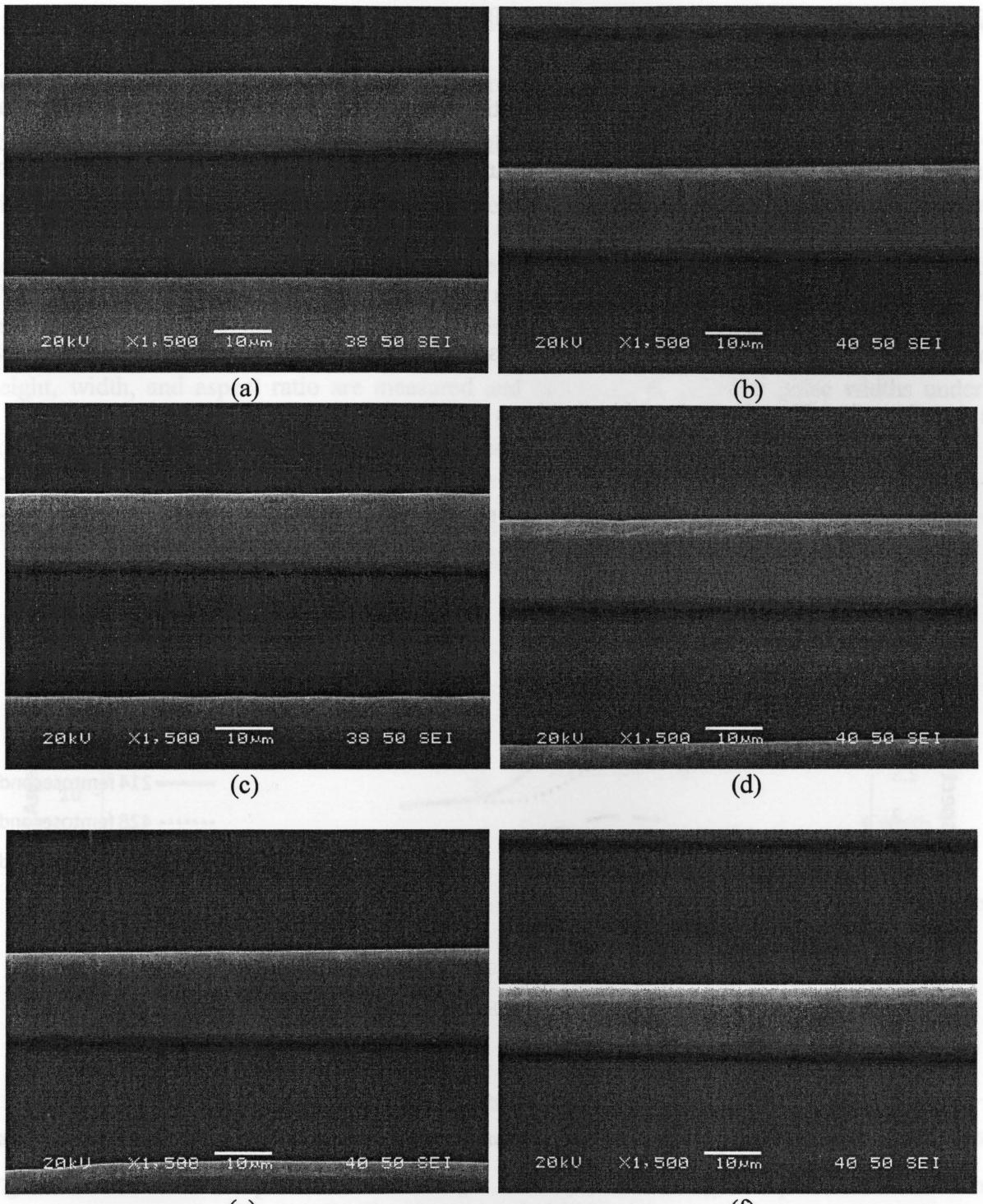


Figure 5-5: Aspect ratio growth at 214 fs pulse width and speed of 5000 µm/s at different values of (a) 2.65 (b) 3.1 (c) 4.7 (d) 3.15 (e) 2.3 (f) 2.29

5.3.2 EFFECT OF PULSE WIDTH ON ASPECT RATIO

Another factor that influences aspect ratio, as shown in Figure 5-6, is pulse width. The curve in this figure is similar to the curve in Figure 5-4 with the addition of multiple pulse widths present for comparison purposes. In terms of a resolution perspective, a transformation from a femto to a pico mode, an increasing pulse width resulted in a decreasing voxel size and in return shown an increase in lateral spatial resolution aspect [53]. However, this idea does not hold true in regards to the affect that pulse width holds on aspect ratio.

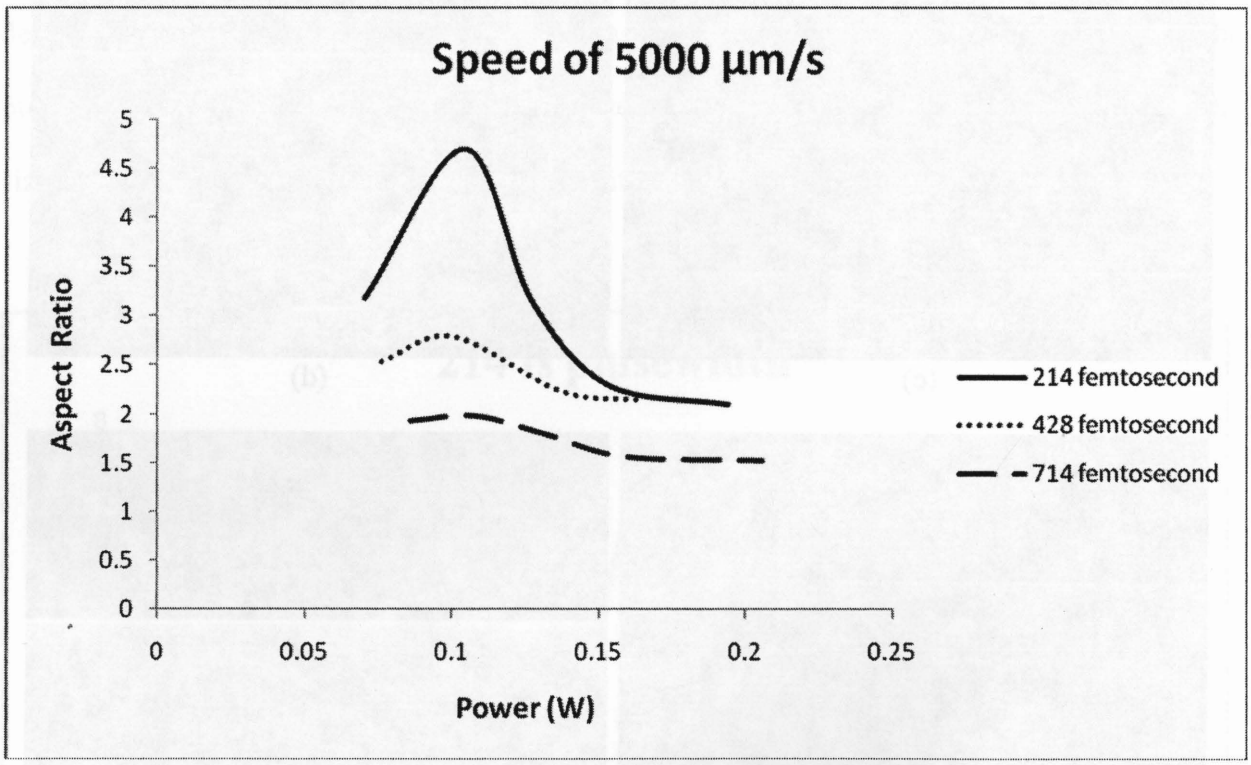


Figure 5-6: The relationship between aspect ratio and laser power at different pulse widths at a speed of 5000 µm/s

From Figure 5-6, it can be observed that although the general curve pattern of the aspect ratio is maintained throughout the different pulse ranges, aspect ratio actually decreases in magnitude as pulse width increases. In order to establish the reasoning behind this occurrence, laser ablation

theory aspect has to be taken into consideration. In a shorter pulse width, the energy deposition occurs on a timescale that is shorter compared to the electron-phonon relaxation time. In addition, the intensity of a short pulse, even with very moderate energy, is high enough to drive highly nonlinear absorption processes in materials that do not normally absorb at the laser wavelength. As a result, structures at higher aspect ratios can be produced by shorter pulse widths under the specified conditions [51, 54, 55]. This fact can also be seen in Figure 5-7, in which height, width, and aspect ratio are measured and compared at different pulse widths under a constant power of 0.104 W and at a constant speed of 5000 μm/s.

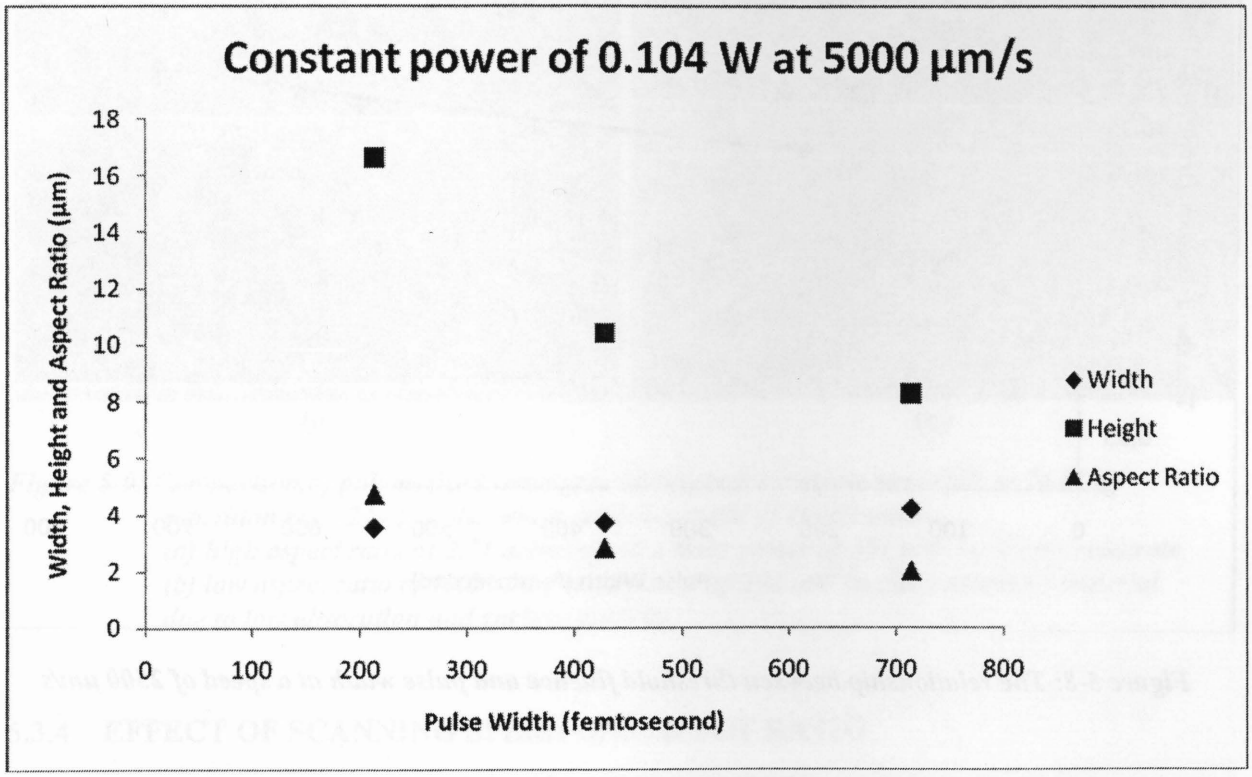


Figure 5-7: The relationship between width, height, and aspect ratio at different pulse widths under a constant power of 0.104 W and at a speed of 5000 μm/s

Polymerization threshold fluence was calculated from the minimum pulse energy required to start 2PP process at the particular combination of pulse width and repetition rate.

These threshold fluence values are plotted against pulse width, as shown in Figure 5-8, and as a result, the relationship between them is clearly established. The threshold fluence is found to increase with the increase in the pulse width from 214 fs to 714 fs. This trend of increase in threshold fluence can be associated with the thermal diffusion of the input pulse energy. The longer the pulse width the more time is available for the heat to diffuse into the bulk before the vaporization stage is achieved [34, 56, 57].

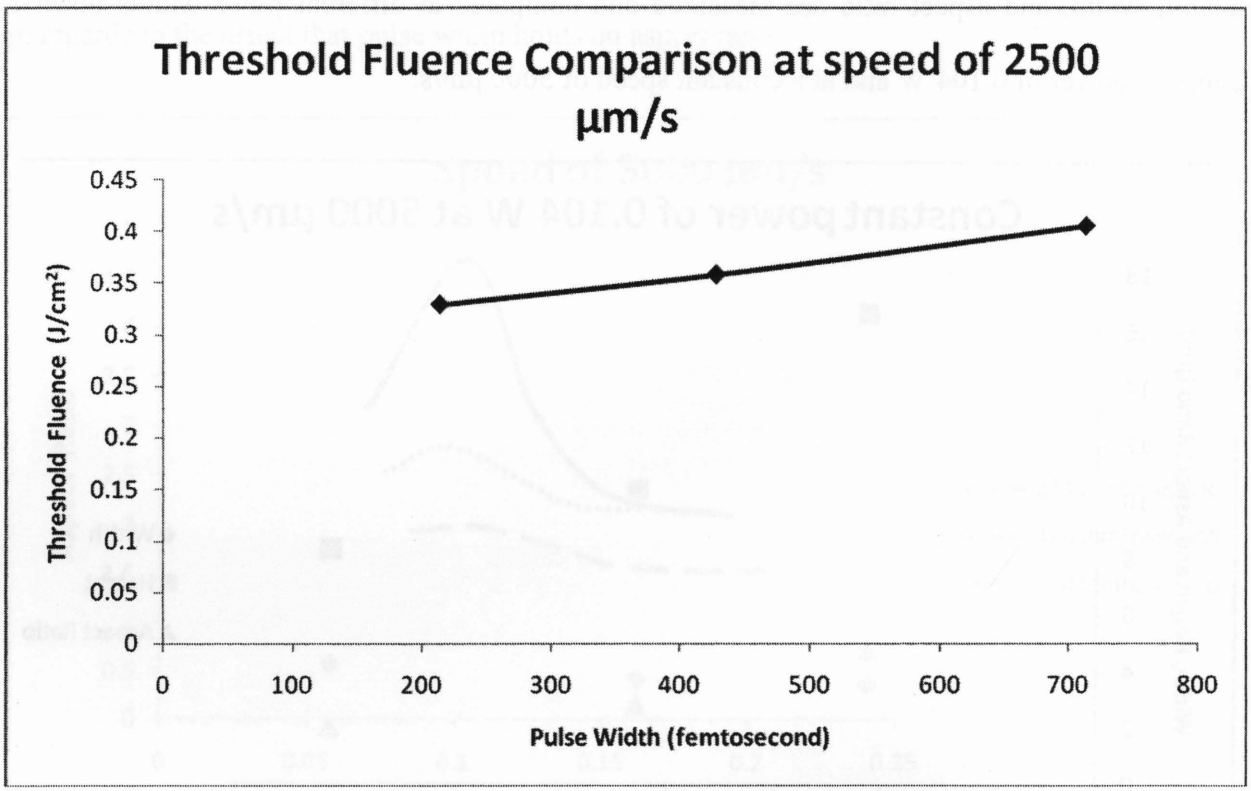
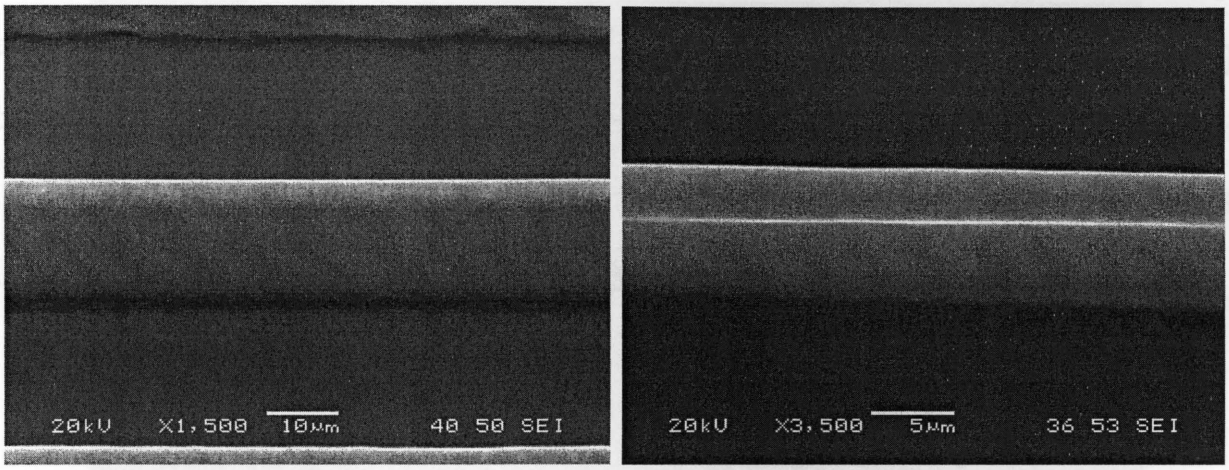


Figure 5-8: The relationship between threshold fluence and pulse width at a speed of 2500 µm/s

5.3.3 EFFECT OF SUBSTRATE MATERIAL ON ASPECT RATIO

Choosing the right substrate material can also play an important role in achieving the highest aspect ratio possible. Although coated with the same photoresist, silicon substrate material exhibited much better results compared to glass substrate material when aspect ratio was

concerned, as can be seen in Figure 5-9. This fact occurs due to the low absorption cross-section coefficient of the glass substrate, which correspondingly limits the possibilities of the 2PP method [58]. In addition, Ormocer photoresist has poor adhesion to a glass substrate due to electrical polarity. Poor adhesion to the glass substrate results in structural failure, such as low aspect ratio, collapse, and low survival rate after the entire 2PP fabrication process [59, 60]. Material's shrinkage has to be optimized as well if the aspect ratio of the polymerized feature is expected to increase.



(a) (b)

Figure 5-9: Comparison of polymerized structures of different substrate materials at 26 MHZ repetition rate, 214 fs pulse width, and at a speed of 10000 µm/s (a) high aspect ratio of 2.71 achieved at a laser power of 301 mW in silicon substrate (b) low aspect ratio of 1.45 at the laser power of 292 mW in glass substrate material due to low absorption and surface polarity

5.3.4 EFFECT OF SCANNING SPEED ON ASPECT RATIO

Another factor that influences aspect ratio is the laser's scanning speed. It has been found that scanning speed is inversely proportional to line width. But the trend is not as obvious as initially presumed due to several limitations present. In general, exposure time increases when scanning speed is reduced. When scanning speed is above a certain minimum value, usually

between 1-10 μm/s, which is untimely dependent on the repetition rate, pulse width, and the laser power used, line width becomes relatively small and it is increased with the decrease of scanning speed. This tendency becomes complicated when the scanning speed becomes high enough so that solidification may not take place because of the low efficiency of TPA due to short exposure time. In addition, when the scanning speed reaches a value below the minimum, the efficiency of TPA is increased and as a result, line width increases dramatically due to the fact that there are so many photons that are absorbed by the resin. It is important to mention that if the scanning speed is increased to a high enough value, disastrous damage due to over exposure can occur [61]. The fact remains that with the increase of scanning speed; increase in width is inevitable and consequently, so is the increase in aspect ratio. The validity of the matter can be confirmed by Figure 5-10, where the slowest scanning speed produces the highest aspect ratio.

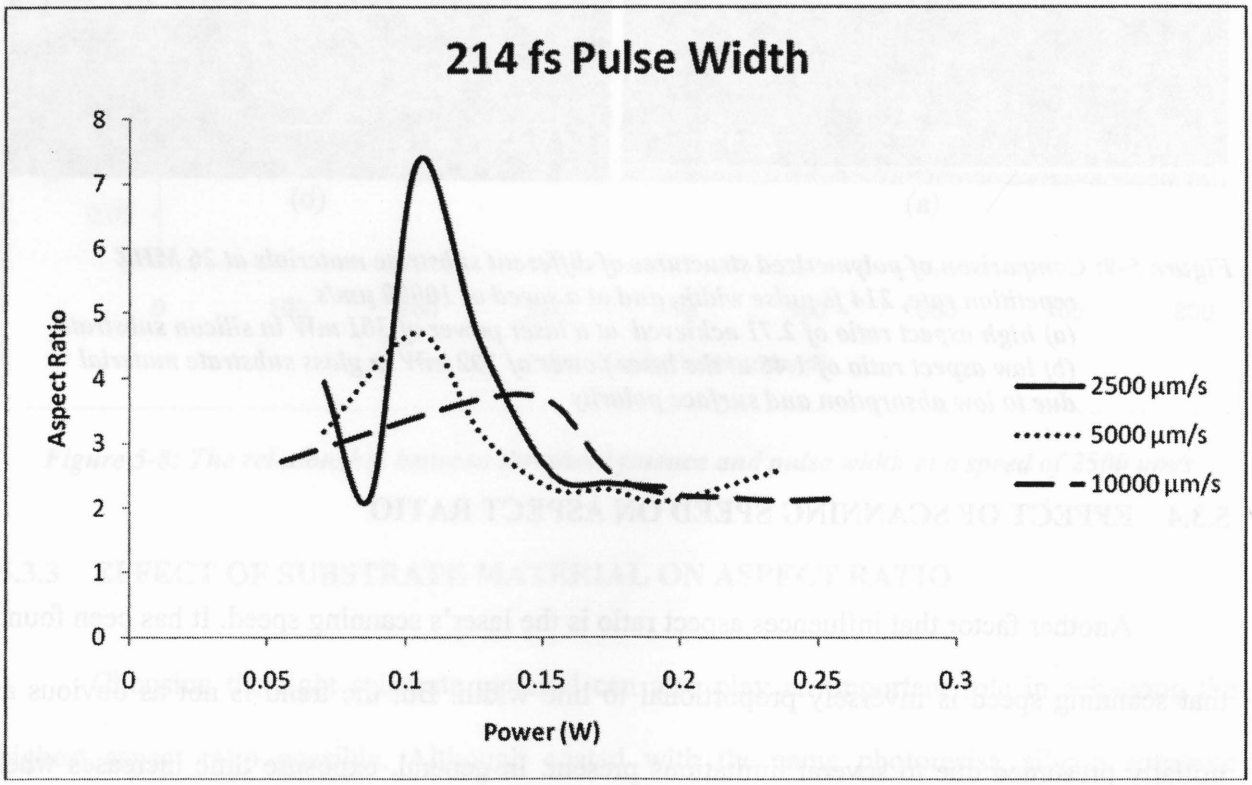


Figure 5-10: The relationship between power and aspect ratio at different scanning speeds at 214 fs pulse width

Another fascinating phenomenon is present in the startling laser manufacturing system. Since the operations of the laser system, such as micromachining and microfabrication, are conducted pixel by pixel (voxel) or point by point formation, small ripples can be observed, as seen in Figure 5-11, depending on the scanning speed [62]. The higher the scanning speed that the piezo scanner operates on, the more ripples would be evident. On the other hand, the slower the scanning speed, the smoother the transition between the ripples and the grooves like features that border them.

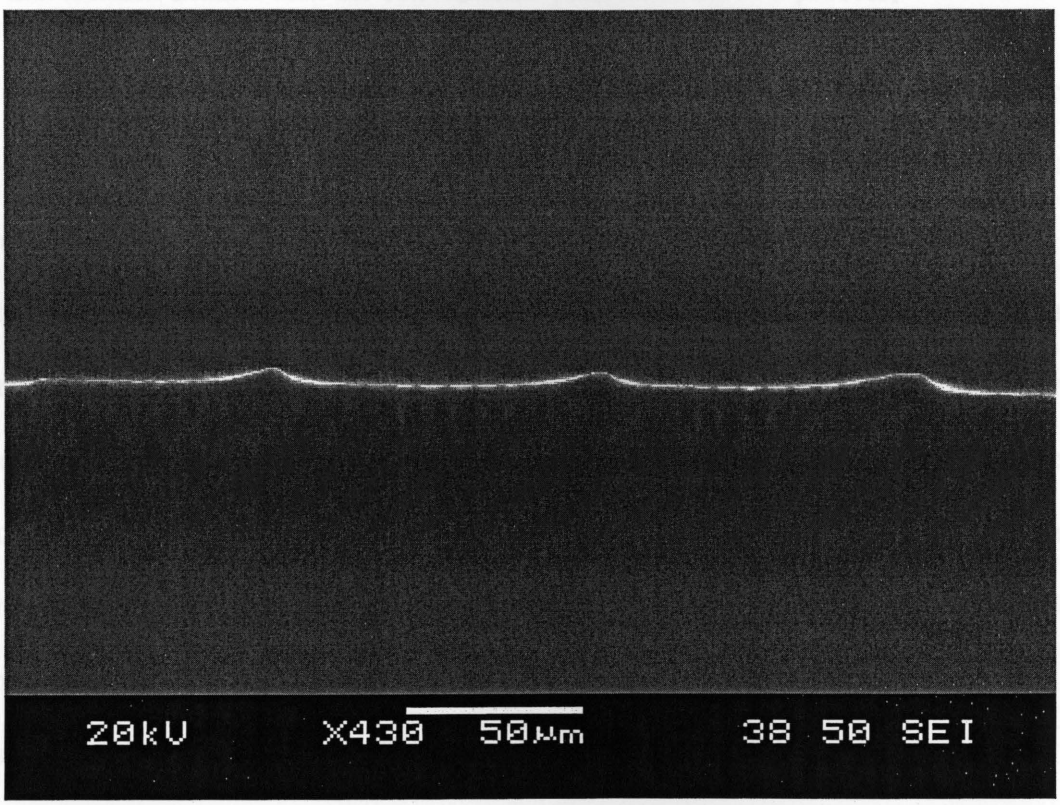


Figure 5-11: Polymerized microstructure showing the effect of scanning speed

5.4 SUMMARY

Although 2PP process is a revolutionary technique and an advancing technology, the influence of aspect ratio has not been properly studied. The factors affecting aspect ratio has

been successfully demonstrated and a small feature size of an aspect ratio of 7.37 has been presented. Aspect ratio has been found to decrease dramatically as pulse width increases. In comparison, as laser power or fluence was increased, the aspect ratio curve tended to increase until a peak was observed. Furthermore, after reaching its peak value, aspect ratio tended to decrease and reach a constant state. Another factor that was found to influence aspect ratio was substrate material. By choosing silicon over glass as a substrate material can increase aspect ratio considerably due to better absorption and adhesion of the photoresist. Glass on the other hand exhibited low absorption cross section and poor absorption due to electrical polarity.

CHAPTER 6

SUMMARY, CONCLUSIONS AND FUTURE WORK

6.1 SUMMARY & CONCLUSIONS

The objective of this research was to employ a new type of laser and utilize the laser's parameters in order to enhance and improve spatial resolution, as well as produce a polymerized feature that is much smaller than the conventional product of the 2PP process.

With the current market demands, which require rapid and efficient production, the single photon polymerization process can not satisfy the requirement of three dimensional micro and nano devices and as a result, becomes an uneven match to its competitors mainly due to the diffraction limit phenomenon. Although the 2PP technique is a relatively new method in micro and nano fabrication, certain groups have already reached a milestone by creating features that are close to 150 nm in size. However, the precision in controlling certain laser parameters in order to produce the smallest feature possible still remains an uncertainty. As a result, choosing the right parameters to control plays an important role in achieving the required resolution and the appropriate feature size. Furthermore, factors affecting spatial resolution have been firmly established but not entirely discussed. Pulse width, for example, still remains an unsolved puzzle that is not entirely conveyed.

For the purpose of conducting experimental analysis for this truly three-dimensional structuring technique, the general models for the current experimental setup were developed after studying the capabilities of the proposed laser system and the necessities of previous investigations in the field. Evaluation of the laser parameters that influence the 2PP process was

justified successfully by performing numerous experiments and examining the results. Several laser parameters such as repetition rate, power, and pulse width were studied in order to measure their influence on feature size.

An experimental analysis was successfully performed on pulse width ranging from 214 fs to 714 fs. These experiments were conducted to emphasize the importance of pulse width on aspect ratio of several polymerized features and on lateral spatial resolution. It has been established that one of the factors that influence lateral spatial resolution is the pulse width, which in response affects polymerization threshold as well. In general, by controlling the laser pulse energy and number of applied pulses, a resolution beyond the diffraction limit can be achieved due to the threshold behavior and nonlinear nature of the 2PP process. Low laser energy, which is at a close range to the polymerization threshold, and short exposure time are the two conditions that have to be satisfied in order to achieve a proper spatial resolution. In addition, it has also been established that an increasing pulse width produces a decreasing voxel size and as a result, increases spatial resolution. Furthermore, it was found that as the pulse width increases, the aspect ratio of the polymerized features decreases.

The experimental results showed that the maximum value of aspect ratio that was able to be produced was 7.37. This aspect ratio value indicates a dramatic increase from the previously known range of 6. The achieved results can be attributed to several factors such as the type of the laser used, which was a high repetition rate-fiber amplified femtosecond laser capable of delivering high power, and the photoresist that was applied. Other factors that contributed to producing features at a high aspect ratio were pulse width and substrate material.

In conclusion, several important contributions were made by this study as outlined:

- Megahertz frequency femtosecond laser has been investigated for the purpose of 2PP process for the first time.

- Slow writing speed, low pulse energy, high repetition rate, and multiple exposures are needed in order to obtain well-defined lines and small size features.

- High aspect ratio can be achieved by implementing silicon substrate material, low pulse width, and slow scanning speed, as well as optimal laser power.

6.2 FUTURE WORK

2PP has become one of the most important methods of multi-photon laser micro and nano-fabrication by which polymer-based optoelectronic and MEMS devices are produced. This process gives rise to spatial resolution due to nonlinear laser-matter interactions by controlling and fabricating features in a spatial volume less than that defined by the optical diffraction limit. As a result, near-field fabrication, which is restrained by the nature of exponential decay of temporary fields and involves two-dimensional structures, can be finally eliminated. However, future research in materials, optics and fabrication of functional devices are needed to further its use in industrial applications.

From an optical perspective, an important task exists in finding suitable mechanisms to construct a parallel production system. This can be accomplished by either a diffraction beam splitter or by a micro-lens array. Usually, the micro-lens array is the preferable way to deal with the situation since further focusing is not needed because of the natural focus that each beamlet endures after passing through the array. The only concern with such a technique is to ensure a uniform power distribution for sensitive control of polymerization from each beam. This is due

to the necessity of mass production since the cost of single beam writing can severely hinder the industrial use of this technology.

The combination of two-photon chromophores, which is part of a molecule responsible for its color, with even higher two-photon absorption cross sections is required when the materials point of view comes into effect. The reason for doing so lies in the high cost of picosecond and nanosecond lasers. This type of synthesis makes photopolymerization feasible for the purpose of commercial applications with less expensive lasers.

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