ABSTRACT


This study primary focuses on identifying the relationship between laser micromachining parameters and the functionality of micro bio-device design. Micro bio-devices such as Lab-on-a-chip (LOC) and microarrays are an emerging technology that recently attracts a lot of attention. For successful applications in the area, the fabrication methods and the system functionality should be addressed. Excimer laser machining is a good candidate to apply to the micro bio-devices manufacturing because different materials can be machined and the process can be easily controlled compared to other fabrication methods.

In the thesis, a parametric study of laser micro machining on different materials are conducted: efforts were focused on identifying the relationship between the laser micromachining parameters and micro bio-device functionality. Experimental study and analytical modeling for the parametric study of excimer laser machining were performed to analyze the machined surface quality and the material removal rate of polyethylene, PMMA and silicon. Microfluidic experiments were carried out to verify liquid flow on laser machined microchannels.

In this study, a novel geometrical model is presented to calculate a contact angle of liquid on the solid substrate to apply for micro bio-device manufacturing. The contact angle can be used to optimize designs of microarrays and microfluidic devices on
development state. Based on a simplified geometry of a droplet, the wetting distance was derived as the function of liquid volume, a contact angle and material properties. To verify our method, the contact angles of a few materials were measured with goniometer, and the results were compared with the contact angle identified by our model. This method can be simplified the current method and the result can be used for design estimation of micro bio-device.

Examples of the proposed technique were presented in the fabrication of inkwells for Dip-Pen Nanolithography (DPN) applications. This study verified that the channel fabricated by laser micromachining allows well-developed liquid flow through the microchannels. The presented methods can be used for laser micro/nano machining of micro bio-devices development and biomedical application.
Analysis and Fabrication of Microfluidic Systems by Excimer Laser Micromachining and Its Applications for Microfluidic and Bio-Medical Devices

by
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DEDICATION

It is dedicated to my late Father, Jaein Kim and my Mother, Yeboon Kim.
BIOGRAPHY

Kim, Eui Seok was born on the west coast of South Korea in 1975. He completed his B.S. degree in Konkuk University in Seoul, Korea and majored in Mechanical Engineering. After receiving his B.S degree, he worked as a research engineer in Dongyang Mechatronics in Korea for a year. In 2005, he started his master degree at Illinois Institute Technology in IL, USA and majored in Mechanical Engineering. After that, he moved to North Carolina State University in 2005 and continues Ph.D degree in Industrial and System Engineering under the guidance of Dr. Yuan-Shin Lee.
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CHAPTER 1
INTRODUCTION

1.1 Research motivation

Micro/nano fabrication methods have been highly developed over the last few decades. Now it is possible to create extremely tiny and advanced structures for various applications. It has realized a lot of things beyond imagination. As an example, a full laboratory in micro scale can be equipped, so call Lab-on-a-Chip (LOC), in the near future. To develop the device, fabrication method as well as system functionality must be carefully considered. There are several methods frequently used to fabricate such devices, including electron beam lithography, optical lithography, nanoimprint lithography, soft lithography, etc. Each method has advantages and disadvantages when it applies to a certain application. Excimer laser micromachining is one of those microfabrication methods. It has been developed in various applications, ranging from medical surgery to semiconductor industry due to its unique advantages. It provides several advantages compared to other microfabrication methods. Most of all, the clearly distinguished advantage is to create microstructures directly using a simply aperture instead of a masking process. Thus, it supports much higher flexibility. Furthermore, unlimited materials ranging from soft tissue to metals can be machining by excimer laser. In general, bio-medical devices are created based on many different materials. Therefore, laser micromachining is a good candidate for fabrication of such devices. On the other
hand, after successfully fabricating of bio-medical devices, system functionality should be verified with a proper method. As an example, if the microstructures involved in the liquid flow, the microfluidic should be examined through the channel. In this study, the application is limited to the microfluidic device. Thus, in the study, the liquid behavior was evaluated in the created structures for the estimation of system functionality. Based on the laser machining parameters and system functionality, the channel geometry related to functionality is linked with laser machining parameters to directly apply laser machining parameters to the system design. Figure 1.1 describes research objective.

![Figure 1.1 Description of research objective](image)

**1.2 Research objectives**

In the research, it primary focuses on the study about the fabrication of microchannels using excimer laser micromachining on polymers and silicon, following
with the parametric study of laser machining. In addition to the parametric study, the liquid flow in the created microchannels is represented by experimental and simulated methods in order to verify and evaluate the design of microchannels. The result is used to link laser machining parameters to system functionality related to the geometry of microchannel. The followings are more detail objectives, divided with several issues.

1) **Parametric study of laser micromachining:** The material removal rate on laser micromachining is dependent on materials and laser parameters. Thus, the different materials must be machined using different machining parameters. The three parameters included laser intensity, aperture size and number of laser pulses is examined on polymers and silicon by the experimental and simulated method. The material removal rate is represented by the depth and width of a microchannel.

2) **Liquid behavior on microchannels created by laser micromachining:** Microchannels created by laser micromachining must allow well developed liquid flow through the channel. Microfluidic experiments are conducted using three different liquids (water, ethanol and glycerine) shown different material properties on the microchannels. The velocity of each liquid is measured to explain the liquid behavior.

3) **The geometrical method to measure contact angles:** The created channel is an open channel because the top of channel is not covered. In the case, the dominant force to allow liquid flow is the surface tension due to difficulty of applied inlet force. For the surface tension driven flow, the contact angle between a liquid and
a channel is an important factor. So, if the contact angle is known, the liquid behavior and the liquid profile in the microchannel can be predicted approximately. In additional, it is a boundary condition for the microfluidic simulation. The geometrical method to measure the contact angle is developed to allow easy accessibility and overcome current issues.

4) Estimated system functionality related to geometries of microchannels and linked the laser parameters and system functionality: The liquid behavior in microchannels with different geometries is evaluated using both experiment and simulation. The channel geometries can be represented by an aspect ratio and a hydraulic radius. The liquid behavior will be estimated on the different aspect ratio and the hydraulic radius. After evaluating the geometrical effect, the system functionality (Channel geometry) is linked to the laser parameters.

5) Develop microfluidic application – Inkwell for DPN (Dip-Pen Nanolithography): The inking method for DPN is still an important issue. The inkwell created by laser micromachining on a silicon substrate. Following experiment - created nanostructures on the silicon substrate - is conducted to verify the inking method.

1.3 Paper organization

This paper is organized as follows.

Chapter 2 introduces excimer laser micromachining including the basic principle and application areas. It also introduces several micro/nano fabrication methods such as
dip-pen nanolithography (DPN). After that, a microchannel is briefly discussed, ranging from the fabrication method and applications, and the experimental and simulated methods for liquid behavior in the channel are introduced.

Chapter 3 demonstrates the parametric study for laser micromachining. Polyethylene, PMMA and silicon are used for the study. After parametric study, the primary microfluidic experiment will be performed on the created channel to verify liquid behavior.

Chapter 4 presents the method to measure a contact angle between a liquid and a solid surface. The droplet geometry on the solid surface is simplified and two math models are derived with and without the gravity effect. In addition, the contact angles calculated by the proposed model and the contact angles measured by goniometer are compared to verify the method.

In Chapter 5, the geometry of microchannels is evaluated. Several different channels are created and liquid behavior is estimated. The geometry of microchannel is represented by an aspect ratio and a hydraulic radius. Finally, the laser parameters are linked to the channel geometry.

Chapter 6 demonstrates the one of microfluidic applications that is an inkwell for DPN. The inkwell creates by laser micromachining and it is utilized to coat the AFM tip. Following nano size structures are generated, combined with wet/dry etchings to verify the inking method.

Chapter 7 concludes and summarizes the results of this study.
CHAPTER 2
LITERATURE REVIEWS

In this chapter, several micro/nano fabrication methods are introduced with concentration on the principle of operation, and excimer laser micromachining is introduced including, operation principles and several applications. Furthermore, advantages and disadvantages of excimer laser for fabrication microstructures will be discussed with comparing to other fabrication methods. Main objective of this study is to create microchannels by laser micromachining for microfluidic applications such as biomedical devices. Thus, microchannels, including fabrication methods and applications are briefly discussed in this chapter. In the last part of this chapter, dip-pen nanolithography is introduced because microfluidic devices created by laser micromachining can be applied to a coating process for dip-pen nanolithography.

2.1 Micro/nano fabrication

Micro/nano structures and systems provide a lot of advantages in various areas because they can contain more functionality in a limited area, and the system size can dramatically decrease. However, it is a challenging problem to create tiny structures and systems in the limited area. Micro/nano fabrication is consisted of material removal, adding and bonding as traditional manufacturing processes. However, due to extremely tiny size of micro/nano systems, traditional process cannot be used for it. In general, nano
fabrication is a more challengeable problem than micro-fabrication because nanostructures are much smaller than microstructures. Wet and dry etchings are the most frequently used method for the fabrication of micro/nano structures. There are a lot of recipes available for various materials [Michael 1999]. Wet chemical etching involves in a chemical interaction between an etchant and a target substrate to remove material and in order to create a certain structure, a masking process is necessary to protect unwanted areas on the substrate. On the other hand, dry etching uses physical bombardment and/or the chemical interaction using plasma technology. It is easy to control the etching parameters and produced much less toxic material compared to wet chemical etching. Plasma etching, reactive ion etching (RIE) and deep reactive ion etching (DRIE) are the major dry etching methods. Dry etching methods also need a masking process such as photolithography, which is mainly used in semiconductor industries. Nanolithography is the fabrication method for the structures usually less than 100nm scale. There are several nanolithography methods. Soft lithography is the fabrication method, using a patterned elastomer as a stamp, mold or mask [Madou 2002]. In general, soft lithography includes microcontact printing (µCP), replica molding (REM), microtransfer molding (µTM), micromolding in capillaries (MIMIC), and solvent-assisted micromolding (SAMIN) and it can create the structures, ranging from 30nm to 100µm [Xia 1998]. Basically, soft lithography uses self-assembly or replicates a pre-fabricated mold.
Tip-based lithography is a relatively new method. Dip-Pen nanolithography (DPN) is the most well-known tip-based nanolithography. To start the process, the target material is coated on the AFM tip and patterned on a certain substrate. On the other hand, nanoscratching is a material removal process with a Diamond AFM tip instead of adding materials [Park 2007]. It is similar to the traditional milling machining. However, it provides very limited accessibility due to the tip geometry (pyramid shape). Anodization nanolithography (ANL) is also the method based on AFM. It was introduced in 1990 [Stiévenard 2006]. When voltage is applied between the AFM tip and the hydrogenated surface, the local oxidation on the silicon surface is grown.

Electron beam lithography (EBL) is a direct writing method without an additional process. It is a material removal process using electron beam. It generally provides very high resolution, less than 10nm [Vieu 2000]. However, it cannot provide a high fabrication rate. Photolithography and X-ray lithography use a light source to fabricate micro/nano structures. Photolithography is the method to transfer a certain structures on the mask.
materials using UV light before etching technology. Currently, it is the most popular method in the semiconductor industries. On the other hand, X-ray lithography uses X-ray to transfer the structures on the base substrate through masks. X-ray has ultra-short wave length, so it allows the structure size to achieve much smaller than the size fabricated by photolithography, however, it does not allow image reduction (usually photolithography allow image reduction- during mask transfer processes). Thus, the mask generation should be a challenging problem especially, when the final shape is extremely small [Madou 2002]. Besides above several processes, a lot of processes for material removal still exist. Furthermore, material adding processes such as chemical vapor deposition (CVD), physical vapor deposition (PVD), pulsed laser deposition (PLD) and spin coating are also used to create micro/nano structures. So far, several micro/nano fabrications methods have been discussed. Every method has advantages and disadvantages. Therefore, proper methods should be selected with careful consideration based on the size, geometries and materials. In the next sub-chapter, a laser based fabrication method is introduced.

2.2 Laser machining technology

Laser machining commonly uses to cut metals, drill a hole such as ink-jet printer nozzles, and directly fabricate micro/nano structures [Gower 2000]. “LASER” stands for Light Amplification by Stimulated Emission of Radiation. Light has different wavelength ranging from 1nm to 1000µm as shown in Figure 2.2. Behind DUV, the x-ray has very short wavelength (0.01nm to 10nm), which is the light source for X-ray lithography.
Laser can be classified with the type of laser sources – solid, gas and semiconductor. In this study, only the gas type laser is discussed.

<table>
<thead>
<tr>
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<th>200nm</th>
<th>400nm</th>
<th>700nm</th>
<th>10µm</th>
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<tbody>
<tr>
<td>DUV</td>
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<tr>
<td>UV</td>
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<tr>
<td>FIR</td>
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</tbody>
</table>

DUV: Deep Ultraviolet
UV: Ultraviolet
NIR: Near infrared
FIR: Far infrared

Figure 2.2 Range of wavelength of light

The gas laser can be classified according to the wavelength. Excimer laser has the wavelength ranging from 157nm to 351nm. On the other hand, ND:YAG has 266nm to 1.06µm wavelength and CO₂ has 10.6µm wavelength. In general, shorter wavelength provides the higher resolution to create structures. Furthermore, the short wavelength laser utilizes laser ablation instead of thermal effect to remove material. On the other hand, longer wavelength laser, including ND:YAG and CO₂ use a thermal effect to create structures. Among three different laser types, excimer is commonly used to create micro/nano structures because higher resolution can be achieved. Laser machining generally provides following advantages compared to other methods. (a) Few processing step, (b) high flexibility, (c) capable of serial and batch-mode production processing, (d) no major investment required, and (e) applicable to a wide range of materials such as polymers, glasses and metals [Gower 2000]. However, the uniform beam quality and the speed of a laser process still need to be improved.
2.2.1 Principle of laser machining

The principle of stimulated emission is used to generate laser [Basting 2005]. Stimulated emission occurs when an electron is in an excited state. When a higher energetic state electron is dropped to a low energetic state electron by passing a photon, the photon with a same wavelength is emitted in the same direction. The laser medium is necessary to emit a photon by stimulated emission. There are four different laser mediums such as gas, solid, semiconductor and liquid. Nd:YAG laser is a one of solid-state lasers. On the other hand, CO\textsubscript{2} and excimer lasers are the gas lasers. Excimer lasers use various gases to generate lasers with different wavelength – F\textsubscript{2}(157nm), ArF(193nm), KrF(248nm), XeCl(308nm) and XeF(351nm). In general, shorter wavelength of light can generate more energy as shown in Equation (2.1).

\[ E = \frac{hc}{\lambda} \]  

(2.1)

E, h, c and \( \lambda \) indicate single photon energy, Planck’s constant, the speed of light and the wavelength of light respectively. There are two operation modes for laser, which are a continuous and pulsed laser. The continuous mode provides continuous energy flow but the pulsed laser transfers varied output energy depended on pulse duration. On the other hand, pulsed laser mode can reduce the thermal effect during the laser process. A general laser machine is consisted of three main components which are laser medium, pumping mechanism and reflectors. A laser medium can be various materials, including gas, solid...
and semiconductor as mentioned before. Pumping makes the medium to be an excited state which has a high electron energy and the reflectors keep simulating the excited electron to emit photons. Figure 2.3 describes the concept and components of laser machine.

![Figure 2.3 The laser components](image)

### 2.2.2 Excimer laser

“Excimer” originated from excited dimer. The first experimental evidence of excimer lasing was obtained by N.G. Basov in 1970 [Basting 2001]. Excimer laser emits ultraviolet and deep ultraviolet. To achieve that, several gases are used as a laser medium. For example, Krypton fluoride (KrF, 248nm), argon fluoride (ArF, 193nm) and xenon chloride (XeCl, 308nm) are commonly used for excimer laser and recently fluorine laser (F₂, 157nm) is successfully applied for micro fabrications [Basting 2005]. Ablation is the most important phenomenon for excimer laser technology. It is characterized by pulse by pulse removal of small amount of materials from the illuminated region of the target with
minimal damage to the surrounding area [Paterson 1999]. Once the target material absorbs the laser energy, the material goes through photochemical (bond breaking by photon absorption) and photothermal (heat induced bond breaking) processes [Saxena 2009]. Laser absorption depends on the material and the wavelength of laser. Generally, higher wavelength decreases the laser absorption. Ablation rate is measured based on Beer’s law. Ablation rate (Ra) can be expressed by absorption coefficient ($\alpha_{\text{eff}}$), laser fluence ($F$) and threshold fluence ($F_{\text{th}}$). When $F$ is larger than $F_{\text{th}}$, the laser ablation occurs. Otherwise, it is not happened. Absorption coefficient and threshold fluence relies on the material type and laser wavelength. Table 2.1 shows the ablation depth according to laser fluence for several different materials. It indicates that the ablation depth can vary with the different fluence and the laser wavelength.

$$Ra = \frac{1}{\alpha_{\text{eff}}} \ln \left( \frac{F}{F_{\text{th}}} \right)$$ (2.2)

The pulse duration is another important factor. Ultrashort laser pulses can minimize a photothermal process during the laser process so that the higher quality structures might be obtained. Especially, melting effects (recast and debris) around the machining areas can be minimized by ultrashort pulses laser. In general, femtosecond laser is ultrashort pulse laser commonly used.
Table 2.1 Ablation depths and fluences according to materials [Basting 2005]

<table>
<thead>
<tr>
<th>Material</th>
<th>Wavelength [nm]</th>
<th>Fluence [J/cm²]</th>
<th>Ablation Depth / Pulse [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate (PC)</td>
<td>248</td>
<td>4.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Polyester (PES)</td>
<td>248</td>
<td>4.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>248</td>
<td>3.7</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>193</td>
<td>6.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Polyimide (PI)</td>
<td>308</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>248</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Alumina</td>
<td>193</td>
<td>45</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>248</td>
<td>45</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>25</td>
<td>0.17</td>
</tr>
<tr>
<td>Zirkonia</td>
<td>248</td>
<td>10</td>
<td>0.12</td>
</tr>
<tr>
<td>Boron nitride</td>
<td>193</td>
<td>20</td>
<td>0.15</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>248</td>
<td>10</td>
<td>0.18</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>248</td>
<td>10</td>
<td>0.13</td>
</tr>
<tr>
<td>Piezoelectric ceramics</td>
<td>248</td>
<td>5.0</td>
<td>0.05</td>
</tr>
<tr>
<td>(PZT)</td>
<td>308</td>
<td>5.4</td>
<td>0.20</td>
</tr>
</tbody>
</table>

As shown in Figure 2.4, the excimer laser can create structures not only by directly fabricating without mask patterns but also by using mask patterns [Zheng 2006, Saxena 2009, Zimmer 2000]. A direct fabricating process usually provides high flexibility and simple implementation. It is the most valuable advantage of laser machining compared to other methods. Typically, micro/nano fabrication methods are consisted of several serial
processes. However, laser machining requires only one single process. On the other hand, it is limited to support a high production rate and high resolution structures. If the mask pattern is used for laser machining, it provides high production rate and creates structures with high resolution. However, more efforts are needed to prepare equipments and operations for the process.

2.2.3 Applications of excimer laser

Recently, there are a lot of applications using laser machining introduced because of its own advantages. As an example, it is used to transfer nanosize patterns on various materials ranging from bio-tissues and metals. In addition, it can create micro size structures using directly writing method as mentioned. Behinds creating micro/nano structures, it can also be applied to medical treatments and traditional industrials. In medical surgery, the minimum invasive treatment and accuracy for cutting a tiny size and

Figure 2.4 Excimer laser processes
removing the small volume of human tissues are the key issues. Especially, some parts of human body such as eye and ear require the issues more than other parts. Excimer laser is used to perform eye, ear and dental surgery [Lubatschowski 2002]. LASIK (Laser in situ Keratomileusis) is the most well-known eye surgery using laser technology. Excimer laser in general reduces the mechanical and thermal stress generated during dental surgery such as drilling and grinding, compared to a traditional turbine-driven drill. Besides the key medical applications, Vitiligo [Hadi 2004] and oral lichen planus [Trehan 2004] and angioplasty can be treated by excimer laser. Currently, there are a lot of industrials and research level applications to create micro/nano structures using excimer laser. It is capable to fabricate from the micro-mould to the microchannel [Khan 2006]. As shown in Figure 2.4 (b), excimer laser is used to create a pattern structures using the patterning mask under laser light. Microfilters consisted of a lot of blind holes were fabricated for microfluidics devices using excimer laser [Saxena 2009]. The mask was fabricated by microdrilling on thin copper sheets and then the pattern was transfer on polyimide substrate. Axially symmetric 3D microstructures were generated by excimer laser with a mask [Lee 2005]. The less opening area has less depth because of less probability for reaching the laser light. It is suitable to generate axially symmetric 3D structures with different depth. The method using a mask pattern supports a high production rate but needs to fabricate a mask. On the other hand, various microstructures such as microchannels are generated using directly writing method with laser machining [Shah 2008]. A microfluidic optical bubble switch consisted of a microchannel and a microheater was fabricated using a direct writing method of ultrashort pulse laser
Microchannel was fabricated on dielectric materials (soda-lime glass and fused quartz) for biomedical device applications because of their thermal properties and chemical stability [Farson 2008]. In the study, they examined the machining parameters influenced on the feature size and quality such as channel depth and surface roughness after machining. In addition, excimer laser machining is widely used for semiconductor industries. For example, it can be used for annealing and texturing for photonic devices [Adikaari 2007].

### 2.3 Microchannel

The main role of microchannel is to delivery liquid for a variety of applications, including a sensor, a bio-medical device and micromolding. A traditional milling machine can create the microchannel with scale down of the process, called micro milling [Bang 2005]. However, it is just capable to scale down at most a few hundred microns. Micro/nano fabrication methods instead of traditional machining processes are generally used to make it. In general, microchannel is classified as an open and a close channel. The close microchannel involves in at least a few serial fabrication methods, including material removal, material deposition and bonding. However, the open channel is just needed to remove material from the top side. Regardless of the channel type, the material is essential to fabricate the microchannel. Therefore, the focus of this study stays on the material removal processes to create channel on a certain material. From the following
sub-chapter, fabrication methods, basic applications and some interesting issues will be presented.

2.3.1 Fabrication of a microchannels

In the paragraph, several fabrication methods are introduced to generate a microchannel. Microchannel is mainly fabricated using traditional micro/nano fabrication methods, which is introduced in the beginning of the chapter. In general, the methods offer very high quality and resolution to create the microchannel. On the other hand, some processes need costly environments and equipments. Wet/dry etching method with a proper masking is frequently used to create microchannels [Verpoorte 2003]. For the wet etching, unwanted areas should be protected with a proper masking, and the unprotected area is etched by a chemical interaction between wet etchant and target materials. It is easy to implement, however, it is an important issue to control etching parameter and toxic materials are involved during the process. On the other hand, dry etching methods such as reactive ion etching (RIE) and deep reactive ion etching (DRIE) does not generate toxic materials during the process and it is also easy to control etching parameters. However, the masking process is not simply, and the restricted environments and expensive equipments are required. Soft lithography is one of the micro/nano fabrication methods using elastomeric stamps or molds. It contains five different processes, which are microcontact printing (μCP), replica molding (REM), microtransfer molding (μTM), microtransfer molding (μTM), micromolding in capillaries (MIMIC),
and solvent-assisted micromolding (SAMIM) [Xia 1998]. It usually generates microchannels with low production cost over other lithography methods. Besides above several fabrication methods, hot embossing and microinjection molding also provide a chance to create the microchannel [Shiu 2008]. Various materials such as silicon, glass and polymer have been used to fabricate the microchannel. However, polymer is most frequently used because they are easy to fabricate and some of them are transparency which provides visibility inside channels. Micro milling process has the same concept of the traditional milling, but is scaled down in micro size. It uses physical contact between a rotating cutting tool and a target material. It does not require very restricted working environment and expensive equipment. It also supports a direct machining method without any masking process, which is similar with laser technology. However, it cannot fabricate very tiny structures (sub-micron) due to the limitation of the equipment and the process. Currently, miniaturized tools down to 50μm diameter have been available [Lee 2005b]. Vibration is another serious issue for micro milling, even small vibration causes a tool broken seriously as well as a process failure, and it is hard to detect the tool broken [Chae 2006]. In addition, brittle materials such as silicon and glass cannot be handled with micro milling.

2.3.2 Studies of liquid behavior through microchannels

The fabrication of microchannel is very important step to create microsystem. On the other hand, the system functionality should be verified. The key issue of microchannel is to transfer liquid from one place to another place without any trouble
such as blocking. To check the liquid behavior in microchannel, a lot of researchers have been working on microfluidic using both experimental and predictive methods. To verify the liquid flow in microchannel, commonly used method is to check the liquid behavior inside the channel during liquid flow. However, it is still challenging to observe liquid behavior in case of an extremely small channel. Besides real experimental studies, the simulation study can be used to predict the liquid behavior. It can save the product development time and find new problems during the product development. However, it is strongly depends on the boundary conditions of physical models and resolution of mesh. Furthermore, it requires the huge computational time for complex and large sized cases. In general, the open microchannel allows liquid flow by surface tension [Chen 2008, Kung 2009]. On the other hand, additional force such as pressure is applied for liquid flow in the close channel [Kim 2002]. Behind the pressure and the surface tension, other forces included the centrifugal force and the electric force. Geometries such as the size of the channels and the turning angle are the other influence factors for the liquid behavior. According to the depth and width of microchannels, the liquid flow was examined [Chen 2008, Kim 2002]. In addition, liquid flow with the different turning angle was also examined and liquid behavior at T junction was studied [Chen 2008, Guillot 2005]. The surface roughness effect was studied by a numerical simulation method [Rawool 2005]. Continuity and momentum equations are basically used to perform the most of microfluidic simulations [Kim 2006, Chen 2008]. However, many cases need to apply different strategies. For the open channel simulation, the effect from the open environment (air) must be considered. Volume of fluid (VOF) method is mainly used
[Hirt 1981]. The method basically uses volume fractional function to calculate the volume ratio between a certain liquid and environmental gas at the different location along the channel. Several commercial codes, including CFD-ACE+, Ansys CFX, Flow-3D and Fluent are available based on the finite volume method. Glatzel et al. compared the performance of commercial computation fluid dynamic (CFD) codes for microfluidic applications [Glatzel 2008].

2.3.3 Applications of microchannels

Microchannel is a fundamental component on various systems such as biomedical devices, sensors and microsystems. Lab-on-a-chip (LOC) is one of biomedical devices containing several laboratory functions in the small size chip. It has a tremendous but unproven potential to improve the health of people in developing countries [Chin 2007]. It might simplify current medical diagnostic procedures such as an allergy test and a certain disease test. A general LOC consists of several microchannels, a mixer and pre-deposited reagents [Haeberle 2007]. Liquid sample collected from outside should be flown through microchannels to pre-deposited reagents for a test. Sometime, mixer is needed to mix a few different samples in the system. For pre-deposited reagents, micro/nano fabrication methods such as tip-based lithography are adopted. All components and functionalities are important to build the chip. However, the most important component is a microchannel because all test materials need to be transferred through the channel to the test area. Several methods are available to allow liquid flow in the channel, such as the capillary force, the centrifugal force, the electrokinetic force and
pressure driven force [Haeberle 2007]. Now, the LOC technology opens a new opportunities and starts to be used commercially. On the other hand, beside the issues of microfluidics, there are still a lot of problems to be improved for more advanced medical applications. For example, the detection method, especially in case of very tiny pre-deposited reagents, is challenging and also digitalization is the key issue. A microchannel is also a main component for a micromolding system. In general, micromolding is used to create microstructures with polymer. Melting polymer is flown into a mold to form a desire shape. In general, the mold contains microchannels and other microstructures. It is a lower cost process over other fabrication methods. Several influenced factors for the size of structures and accuracy, including mold temperature, melting temperature, injection velocity and packing pressure were examined by Chien [Chien 2006]. The study applied micromolding for fabrication of biochip devices.

2.4 Dip-Pen Nanolithography (DPN)

2.4.1 Introduction to DPN

Dip-Pen nanolithography is a direct writing process with a coated Atomic Force Microscopy (AFM) tip on the substrate in micro/nano scale. It was invented by Dr. Mirkin's group in 1999 [Piner 1999]. They created nano structures and patterns with a combination of alkanethiols and a gold thin film, and the highest resolution achieved was less than 20nm. DPN has been developed to pattern various materials, including small organic molecules, polymers, DNA, proteins, peptides colloidal nano-particles, metal
ions and sols. Also, the range of patterning substrates has been expanded to cover many insulating, semiconducting and metallic substrates [Salaita 2007]. In general, for the DPN process, the AFM is operated in a contact mode and a certain material coated on the probe tip is transferred to the surface of substrate through water meniscus which is generated between the AFM tip and the substrate due to humidity in ambient conditions. Figure 2.5 describes the basic concept and mechanism of DPN. Once the material is transferred to the substrate, it starts to diffuse on it. Thus, it is a very critical issue to know influencing factors for the diffusion during the process. There are several critical factors that affect the diffusion rate during DPN process. The most influential factor is a chemical interaction between the ink and the substrate because the ink cannot be stable on the substrate without a suitable chemical interaction. Behind the chemical interaction a coating method, a writing speed, a tip size, humidity, temperature and surface roughness also have influences on the diffusion rate.

Figure 2.5 Description of dip-pen nanolithography
A current drawback of DPN is low repeatability and the low operation rate compared to other methods. For higher repeatability, the influenced factors should be controlled with careful consideration. Numerous researchers have been trying to create parallel DPN systems with multiple tips to overcome the low operation rate. Currently, 55,000 tip-cantilever across a 1cm² chip is fabricated and achieved of $3 \times 10^7 \mu m^2$/hour production rate [Haaheim 2008].

2.4.2 Applications of DPN

Since DPN was introduced, a lot of researchers have tried to apply DPN in various research areas because of the remarkable benefits of AFM such as a simple and flexible operation. DPN can substitute current nanolithography methods very successfully in certain areas. A few application areas are presented in this chapter.

1) Resist for wet and dry chemical etching

DPN has successfully deposited self assembly monolayers (SAM) with 16-mercaptohexadecanoic acid (MHA) or 1-octadecanethiol (ODT) on gold, silver and palladium substrate, and SAM can be used as a resist for wet etching [Weinberger 2000, Zhang 2004]. The MHA and ODT patterns protect substrates against wet chemical etching. Combinations of an ink and a substrate for DPN are very similar with the solution of micro/nano contact printing. It is probably possible to substitute micro/nano contact printing (μcm) as DPN if a high operation rate of DPN is achieved. The method can be used to generate pattern resists for dried etching methods such as reactive ion
etching (RIE) [Zhang 2007]. For example, DPN generates patterns on silicon wafer coated with titanium and gold. A thin layer of titanium and gold are etched out using wet chemical etching after pattern generation. Remaining gold patterns play as resists during reactive ion etching which then transfers patterns onto a silicon substrate. Above methods can only generate positive structures. However, generations of negative structures with DPN has been reported [Wei 2007]. They created 1-octadecylamine (ODA) pattern on a gold substrate and passivated non-patterning areas with MHA. The ODA pattern was selectively removed with chemical etching successfully. Figure 2.6 shows the positive and negative etching.

![Figure 2.6 Positive and negative etching](image)

2) Micro/nano protein bioarray generation

DPN can pattern bio-material such as protein on substrates. In general, it uses direct and indirect deposit methods. For the direct method, it must generate the linker array to immobilize the protein array and after that, DPN transfers protein to the substrate
directly. Indirect method patterns linker layer using DPN and immerses the substrate into a liquid based protein. Each method has its own advantages. For example, the direct method can generate more complex structures with multiple proteins, whereas, the indirect method more easily maintains bioactivity of protein during patterning processes. The miniaturized protein array is very important for proteomics and cell research [Lee 2002]. Particularly, medical diagnostic and drug development have used the micro/nano protein arrays. Several different strategies for bio-material patterning can be available with DPN [Kim 2010a].

3) **Pattern generation with nanoparticles**

Recently, many researchers have been working on deposit nanoparticles on substrates because of the tremendous applications such as a nanoscale sensor. The strategy to deposit nanoparticles is exactly the same as patterning protein arrays. In general, there are two approaches. The first approach is generating patterns with organic material using DPN and then dipping the pattern into nanoparticles. The patterns of organic material can hold nanoparticles on it. It can create a very thin layer or monolayer of particles on the substrate. On the other hand, the pattern size depends on the diffusion rate of organic materials, but cannot be controlled with the diffusion rate of particles. Additionally, it takes a very long time to absorb nanoparticles on organic patterns. The other method is to directly deposit nanoparticles on substrates [Roy 2007]. The size of patterns of nanoparticles can be controlled directly using a different size of the scanning
area. However, the thickness is very hard to control. This demonstrates that uniform thickness and size are rarely achieved using direct deposit with DPN.

Behind the above three main applications, there are still many possible applications. However to develop more applications with DPN, a high speed DPN system must be developed. A parallel DPN system has been developed [Hong 2000, Bullen 2003, Haaheim 2008]. Furthermore, there are several process related to DPN. The processes share the primary concept of DPN and just change the concept of operation such as applying voltage, using diamond tip to use it for other purposes. They can be used various applications such as material removal with a physical contact and deposition of molten metals.

2.5 Summary

In this chapter, excimer laser micromachining is briefly introduced, included the basic principle and applications. Excimer laser, especially a direct writing method offers a lot of advantages compared to other fabrication methods, which are easy to implement, simple working environment and easy to change a process according to different designs. After discussing about excimer laser micromachining, microchannels were introduced with the fabrication methods and current applications. Furthermore, the method to estimate the microchannel functionality was discussed using predictive and experimental methods. In the last part of this chapter, DPN was briefly introduced with the concepts and current applications.
CHAPTER 3

FABRICATION OF A MICROCHANNEL USING EXCIMER LASER MICROMACHINING AND LIQUID FLOW THROUGH THE MICROCHANNEL

The present study focuses on excimer laser micromachining to create microstructures and the experimental observation of liquid flow through the microchannel created by excimer laser micromachining (ArF, 193nm). Current fabrication methods of microchannels generally require serial fabrication processes and are hard to fabricate different depths of channels on the same system. To overcome the drawbacks, laser micromachining was applied to create microchannels. This chapter contains a parametric study of excimer laser micromachining for three materials – polyethylene, PMMA and silicon. Microchannels were created on the materials with proper machining parameters based on the parametric study and analytical modeling. After generating microchannels, in order to verify successful liquid flow in the channel, microfluidic experiments were performed with a few different liquids. Glycerin, water, and ethanol were used for testing. The liquid fluid was visualized using fluorescent dye and the velocity was calculated for each liquid flow to compare the liquid behavior.
3.1 Introduction

Micro/nano fabrication methods have made possible the creation of extremely tiny structures and systems which cannot be generated using traditional manufacturing processes. In general, a denser structure in a limited area can provide more functions for a system. A highly functional device in a limited area can be accomplished using micro/nano fabrication methods. There are several methods frequently used, including X-ray lithography, electron beam lithography, tip-based lithography, photolithography, wet/dry etchings and laser technology. Each method has its own advantages and disadvantages according to the intended application. Most methods generally need a masking process for the selective removal of material. A few processes, such as electron beam lithography and laser micromachining, do not require a masking process because they have the capability to directly fabricate structures on various materials. Laser micromachining is one of micro-fabrication methods and it applies in various areas included semiconductor industries and biomedical industries. Different complex geometric structures can be easily created with the method.

A microchannel is a tiny channel to delivery liquid for certain functionality in microsystems. It may be used in various applications, ranging from applications in manufacturing industries, such as micromolding and printer nozzles, to biomedical devices for medical diagnostics, such as LOC (lab-on-a-chip) or μTAS (micro total analysis system) [Kim 2002, Dittrich 2006]. Microchannels are mainly classified as either open channels or closed channels. An open channel, in general, has an open top part; a closed channel does not have any open parts. The closed microchannel demands more
complicated serial fabrication strategy. A microchannel is generally created by micro/nano fabrication. However, other methods such as micromilling are also used, according to the size of the system. Currently, wet/dry etching is the most popular method to fabricate microchannels; in particular, deep reactive ion etching can be used to create the channels, giving a high aspect ratio compared to other methods, and various materials, ranging from silicon to glass, are etched using this method [de Boer 2000]. However, deep reactive ion etching requires additional masking processes using organic layers, photoresists or metals. Additionally, it is very hard to create channels with different depths on the same system. Soft lithography, including microcontact printing (µCP) and a few different micromolding methods, can also be used to fabricate the microchannel [Rosqvist 2002]. It creates micro-structures by replicating prefabricated mold structures using certain materials, such as a molten polymer. Thus, it is relatively low-cost and suitable for mass production. However, the range of materials that can be used for soft lithography processes are limited because of the nature of the process. The methods introduced above need serial fabrication steps, not a single process. Meanwhile, excimer laser micromachining can create microchannels directly on various substrates [Shah 2008, Zheng 2006]. The resolution of structures created by laser micromachining is mainly dependent upon the wavelength of laser. It offers several advantages compared to other fabrication methods. First, it is easy to implement by controlling a few parameters. Second, it does not require complicated serial processes and a restricted working environment such as masking and coating processes in a clean room facility. Third, the geometry of a structure can be easily controlled with simple tool path codes, which are
those used for traditional CNC machining. It makes the geometries of microchannels easily changed, based on the design, simply by using a different tool path. Meanwhile, Micro/nano fabrication should recreate a mask or a mold structure whenever the design is changed. In addition to above benefits, it can prevent contamination during the process because it does not need to directly contact to the substrate.

![Fabrication methods for a microchannel](image)

Figure 3.1 Fabrication methods for a microchannel
Although the laser method demands a long machining time to fabricate a structure with a high aspect ratio and a large area (however, it can be controlled by laser specifications such as laser energy and frequency), it is a good method to create a microstructure. Figure 3.1 describes a few microfabrication processes to create microchannels.

For successful applications of microchannels, a well-developed liquid flow in the channel should be verified. Without proper liquid flow, no result can be acquired from the microfluidic system. Liquid flow in a microchannel shows a significantly different phenomenon than flow in a normal scale channel, because the dominant forces for liquid flow are completely different in micro scale. The normal scale channel is, in general, driven by gravity and pressure; liquid flows from a higher location and higher pressure to a lower location and lower pressure. However, gravity is negligible in most microchannels. To allow liquid flow in the microchannel, the surface tension, the centrifugal force, the inlet pressure and electrokinetic transport are manipulated. The centrifugal force is applied to the microchannel by means of rotating the base substrate [Maruyama 2008, Madou 2001]. Once the base substrate starts to rotate, the liquid is transferred from a reservoir, located at the center of rotation, through the microchannel to the target area at near the edge of the substrate. Applying pressure at the inlet is another method to develop liquid flow [Ismagilov 2001, Dutta 2006]. During pressure-driven flow, the bulging of microfluidic system is a challenging problem [Holden 2003]. Generally, pressure is applied for a material with high viscosity, such as molten polymer during microinjection molding. Electrokinetic transport (electroosmotic flow) is the final mechanism for flowing liquids through a microchannel. Silicon, polymers and glass are
generally used to create the microchannel that uses an electrokinetic transport mechanism. To achieve a microfluidic system with electrokinetic transport, the surfaces of microchannels are charged negatively, and a positively charged liquid forms an electric double layer on the microchannel. Once an electric potential is applied along the microchannel, the positively charged liquid molecules, attracted by electrostatic forces, move toward the negative electrode [Haeberle 2007]. The above three forces for liquid flow are external forces. Surface tension, on the other hand, is a force which acts between liquid and its environment. This means that it is one of material properties between liquid and solid surface, an intrinsic instead of an extrinsic force. Surface tension is usually the dominant force driving liquid flow in an open channel. Many studies have been examining microfluidic conditions using both experiments and simulation methods [Kim 2002, Chen 2008, Kung 2009]. In order to verify a well-developed liquid flow in a microchannel, the most important thing is to visualize the liquid flow during experiments using a proper method. In this research, only the case of an open microchannel will be handled. Thus, the dominant force in the channel will be the surface tension.

In this chapter, a method to create microchannels with laser micromachining is introduced on three different materials – silicon, PMMA (polymethylmethacrylate) and polyethylene. The study contains the evaluation of machining parameters of laser micromachining and analytical modeling to create a desired shape. In addition, microfluidic conditions in the fabricated channels will be examined with a few different liquids (ethanol, water and glycerine). Liquid flow will be visualized with fluorescent dye and UV black light. The velocity will be calculated for each case, comparing between
different liquids to represent the liquid behavior. The chapter will be organized as follows. Excimer laser micromachining technique will be demonstrated for the fabrication of the channel and parametric study. Then, liquid flow will be evaluated with a few different liquids. In the last part, the results of the experiments will be discussed.

3.2 Fabrication of microchannels using laser micromachining

3.2.1 Setup of laser micromachining

Laser micromachining can directly fabricate microstructures without additional processes, such as masking. Some materials are challenging to handle with a particular micro/nano fabrication method. Laser micromachining, on the other hand, can machine various materials, including glass, polymers, semiconductors, metals and bio-tissues [Dyer 2003, Sugioka 2005]. Several parameters, including feed rate, energy level, laser frequency, number of tool paths and aperture size, should be controlled to create the desired structure.

Figure 3.2 Excimer laser micromachining system
In this research, excimer laser (193nm, ArF, 25 nanosecond, Max energy: 400mJ, and Max frequency: 10Hz), which is a lab-built micromachining system consisting of a commercial laser scriber (COMPexPro 201, Coherent Inc.), a 3-axis micropositioning stage (A320, Aerotech Inc.) was used and CAD/CAM module to control the design of structures. Figure 3.2 shows the laser micromachining system. The micropositioning stage is controlled by a G-code system as is used for numerical control machine tools. Laser micromachining provides high flexibility and is easy to implement compared to other fabrication methods. The system can fabricates structures directly without a mask pattern as well as transfer a masking pattern like other fabrication methods. However, in this study, an aperture is used to create a single laser spot on the substrate, and the laser spot creates structures along the G-code tool path in this research.

3.2.2 Laser parametric study with experiments

The dimensions of the structure created by laser machining can be controlled using several parameters. The material removal rate on laser machining is varied by material. In this chapter, several machining parameters are checked to evaluate material removal rate on different materials. Numerous studies have been conducted on the machining parameters for an excimer laser process as well as the material properties that influence laser machining [Liu 1997, Zhang 2001, Amer 2005, Hauer, 2002, Pham 2002]. In general, different materials show different material removal rate from laser machining, even with exactly the same machining parameters. In this study, the parametric study was performed with silicon (100), polyethylene and PMMA.
In this study, the primary parameters about laser micromachining were examined. The results are represented as the depth and width of a microchannel. Other parameters were fixed during the experiment. Before the experiment is described, the laser profile, an important issue for the created shape, should be discussed. The laser beam profile generally follows a nearly Gaussian distribution, as shown in Figure 3.3. Thus, the created channel exhibits as a Gaussian distribution shape. The largest depth happens at the center of microchannels, gradually decreasing out from the center of the channel. The beam profile can be improved to a top-hat profile or uniform distribution with homogenizer lenses. The most well-known homogenizer is a fly-eye homogenizer [Basting 2005]. It consists of two arrays of polished cylindrical lenses set at a prescribed distance. The first array separates the laser beam, and the second set of lenses overlaps the separated laser beams onto the focal plane. Another homogenizer was introduced in 1999. It splits the laser beam into two parts, and then inverts one of those parts [Jasper 1999]. When two parts of a laser beam are overlapped, the top-hat laser profile is generated.

Figure 3.3 Gaussian laser beam profile
3.2.2.1 Aperture size

To create microstructures on a material, a simple aperture is used to transfer a laser beam. A1, A2 and A3 indicate the different aperture size. Figure 3.4 shows the spot area according to the aperture size. The aperture is a circular shape (A1=3.7×10^-4 cm², A2=4.6×10^-4 cm² and A3=5.4×10^-4 cm²).

![Figure 3.4 Spot area according to aperture sizes](image)

3.2.2.2 Actual laser energy on the substrate

Due to laser delivery system, the most input laser energy is lost during the process. Thus, only a small portion of laser energy will reach to the substrate. Actual
laser energy is measured on the substrate by using a power meter. Actual laser measured instead of input energy gives real contribution to remove materials. The actual laser energy increases as aperture size becomes larger and the input energy increases.

3.2.2.3 Cutting width of materials

The cutting width mainly depends on the aperture size and laser density. So, even if the aperture sizes are the same, but the cutting widths are different with the different laser density. Furthermore, the cutting width slightly increases as number of laser pulses increases. Figures 3.6, 3.7 and 3.8 show the cutting width on the different materials – polyethylene, PMMA and silicon.
Figure 3.6 Cutting width according to the aperture size and laser energy on polyethylene

(a) Cutting width with A2

(b) Cutting width with A3
Figure 3.7 Cutting width according to the aperture size and laser energy on PMMA
Figure 3.8 Cutting width according to the aperture size and laser energy on silicon (100)
3.2.2.4 Cutting depth of materials

The cutting depth depends on the aperture size, laser density and numbers of pulse per unit area as same as the cutting width. Figures 3.9, 3.10 and 3.11 show the cutting depth on the different materials – polyethylene, PMMA and silicon. Cutting depth increases in most cases as number of laser pulses increases.
Figure 3.9 Cutting depth according to the aperture size and laser energy on polyethylene

(a) Cutting depth with A2

(b) Cutting width with A3
Figure 3.10 Cutting depth according to the aperture size and laser energy on PMMA.
Figure 3.11 Cutting depth according to the aperture size and laser energy on silicon (100)
3.2.2.5 Results and discussion of experiments

During the experiment, laser frequency and the feed rate maintain a constant value. Relatively high feed rate was used. The laser spot size can be controlled by the aperture size. A larger aperture size means a larger exposure of the laser beam on the substrate. All factors mentioned above are related with the laser pulse per area. So the material removal can be predicted by number of laser pulses per area and laser intensity of each single pulse. Figure 3.12 shows the images of the created channels on three different materials. Among three materials, the channel on polyethylene has highly smooth surface and clear images. On the channel fabricated on the silicon substrate, however, a lot of debris and recasts were observed. The surface finish should be improved with proper methods [Wongwiwat 2010]. Figures 3.6 through 3.11 present the depth and width of the microchannel on three different materials, according to different machining parameters. Most of the results indicate that higher energy increases the cutting depth as well as the cutting width. Furthermore, larger aperture size tends to create deeper and wider channels compared to a smaller size aperture. As the number of laser pulses increased, the cutting depth significantly increased, but the width slightly increased compared to the depth for all materials. With the same aperture, the same energy and the same number of laser pulses, polyethylene shows the largest depth. The channel on silicon, by contrast, represents the smallest depth among three materials. Figures 3.8 and 3.11 indicate that the depth and the width of a channel on silicon increase as the aperture, the energy and number of laser pulses increase. Among the three factors, the aperture is the strongest factor influencing the material removal rate. On the other
hand, with a low energy level, it is hard to create a high depth of channel. It demands tremendous machining time. In general, a high energy level is required for silicon. Furthermore, cutting depth of silicon does not show the perfect linear relationship. It may come from the unknown effect such as thermal effect during the machining. UV photons below material threshold value heats the materials and give heating effect. Silicon has highest threshold value, so it has more thermal effect. In case of polyethylene, channel width dramatically increases as the aperture size increases. Meanwhile, cutting depth is slightly influenced by the aperture size. Changing the energy level does not provide a significant effect on polyethylene. However, the cutting depth is not much different from the values at higher energy levels. For most cases, number of laser pulses does not have a strong effect on the width of a microchannel as it does on the depth. In this study, only these three parameters were checked before the fabrication of a real microchannel system. Different materials showed different results with the same parameter change. In order to control the geometry, including the depth and the width, proper parameters must be selected. Table 3.1 is the summary of the effect of laser machining parameters. The effect of machining parameter was compared on the same material but not on the different material. When the design of microchannel is decided, optimized machining parameter should be selected to fabricate the desired geometry. For examples, the width of microchannel should be controlled by the aperture size and laser intensity. On the other hand, the depth should be manipulated by laser intensity and/or number of laser pulses.
Figure 3.12 Created channels on three different materials
Table 3.1 The effect of laser machining parameters

<table>
<thead>
<tr>
<th>Material</th>
<th>Laser energy</th>
<th>Aperture Size</th>
<th>Number of repetitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Depth</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Depth</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>PMMA</td>
<td>Depth</td>
<td>High</td>
<td>Mediate</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

*Each parameter is compared on the same material.

3.2.3 Selection of laser parameter according to the design of microchannel

Equation (3.1) indicates the material removal rate based on Beer’s law (Equation (2.2)). \( \alpha \), \( F_{\text{max}} \), \( F_{\text{th}} \) and \( \sigma \) indicate on absorption coefficient, maximum laser fluence (F), threshold fluence of material, and the range of laser beam spread (=\( W/6 \), \( W \) is the width of channel). The equation shows the removal depth per a single laser pulse. Figure 3.13 represents the channel profile according to the laser distribution to select the machining parameters. The highest depth happens at the center of channels as Equation (3.2). The ablation depth of material according to the laser pulse was examined [Ren 2009]. The channel width (D) is represented with Equation (3.3). \( \theta \) indicates the slope of laser beam. The new beam width and channel depth (\( d_{\text{max}} \)) due to pulse overlap can be represented by Equation (3.4) and (3.5). First of all, the aperture size and laser intensity must be selected based on the channel width. Once the aperture and laser intensity are selected, number of
laser pulses per area can be estimated with a given maximum channel depth. At the last step, the detail laser parameters can be evaluated with the estimated number of laser pulses. Figure 3.14 describes the procedure.

![Diagram](image)

**Figure 3.13** Channel profile according to the laser energy distribution and the laser energy shape

\[
d(x) = \frac{1}{\alpha} \left( \ln \frac{F_{\text{max}}}{F_{\text{th}}} - \frac{x^2}{2\sigma^2} \right)
\]

(3.1)

\[
d_{\text{max}} = \frac{1}{\alpha} \ln \frac{F_{\text{max}}}{F_{\text{th}}} \quad \text{(at } x = 0)\]

(3.2)

\[
D = 2\sigma \sqrt{2 \ln \frac{F_{\text{max}}}{F_{\text{th}}}}
\]

(3.3)

\[
W_n = W + (d_{\text{max}})_{n-1} \tan \theta
\]

(3.4)
\[(d_{\text{max}})_n = (d_{\text{max}})_{n-1} + \frac{1}{\alpha} \left( \ln \frac{WF_{\text{max}}}{W_n F_{\text{th}}} \right) \] (3.5)

Figure 3.14 Flow chart to estimate laser machining parameters

Figure 3.15 compares between experimental and simulated methods for the laser parameters on polyethylene.
Figure 3.15 Cutting depth (simulation and experiment) with different laser energy and number of laser pulses per area for Excimer laser micromachining on polyethylene.

### 3.2.4 Fabrication of a microchannel system using laser micromachining

Silicon (100), polyethylene and PMMA were used to fabricate microchannel systems. Before laser machining, silicon was cleaned by both acetone and methanol in an ultrasonic bath, and both polyethylene and PMMA were cleaned by methanol in an ultrasonic bath. The machining parameters were selected through careful consideration about the results of the parametric study. Simple microchannel systems consisting of a single microchannel and a reservoir on the inlet side are created. Figures 3.16 and 3.17
show the design of microfluidic system and the images after fabrication by laser machining. The length of the microchannel is 9mm and the diameter of the reservoir is 3mm. The reservoirs on both polyethylene and PMMA were created by a conventional milling process to save the fabrication time for a larger part. During the fabrication, the reservoir was created firstly and then fabricated the channel to prevent blocking effect by the milling process. However, the reservoir on silicon was created with only excimer laser machining because it is not a suitable material for the traditional milling process. The reservoirs on polyethylene and PMMA can preserve a considerable volume of liquid. On the other hand, the reservoir on silicon can store only a tiny volume in sub-microliter.

Figure 3.16 The design of the microchannel system
3.3 Liquid flow through a microchannel

3.3.1 Background of liquid flow

It is known that viscosity is the main variable contributing to the development of liquid flow in a microchannel [Kim 2002]. In general, shear stress is generated against liquid flow in proportion to a viscosity coefficient, as in Equation (3.5). $\tau$, $\mu$, $u$ and $y$ indicate shear stress, viscosity, velocity and the flow direction, respectively.

$$\tau = \mu \frac{\partial u}{\partial y}$$  \hspace{1cm} (3.5)

The liquid behavior in the microchannel can be explained by a model of the capillary effect in a capillary tube [Kim 1995, de Gennes 2004].
\[ F_{\text{surface}} - W_g = F_\mu \]  \hfill (3.6)

\( F_{\text{surface}} \) is the driving force by the surface tension, \( W_g \) is the weight of liquid in a vertical capillary tube, and \( F_\mu \) is the viscous friction force. For a horizontal channel, the weight can be neglected. Therefore, the model is expressed with the following equations.

\[ F_{\text{surface}} = F_\mu \]  \hfill (3.7)

\[ F_{\text{surface}} = 2\pi R_h \gamma \cos \theta \]  \hfill (3.8)

\[ F_\mu = 8\pi \mu V y \]  \hfill (3.9)

Where,

\( R_h \) = hydraulic radius (the ration between the area and the wetting distance of the section of a microchannel)

\( \gamma \) = surface tension of liquid/gas interface

\( \theta \) = contact angle of liquid on the solid substrate

\( V \) = velocity of liquid (dy/dt)

\( y \) = moving distance of liquid

Thus, by substitution of Equations (3.8) and (3.9) into Equation (3.7) One can get the following equation.

\[ \frac{dy}{dt} \approx \frac{R_h \gamma \cos \theta}{4\mu y} \]  \hfill (3.10)
Equation (3.10) demonstrates the general case for a closed capillary tube. However, it may be applied to an open microchannel, at least to see the influence of each parameter, instead of the exact value. The equation indicates that the velocity of liquid increases with high surface tension and a low contact angle. Additionally, based on Equation (3.10), a high hydraulic radius provides a high velocity of liquid flow. On the other hand, high viscosity makes the velocity smaller, and the velocity decreases as the liquid travels through a channel.

3.3.2 Experimental setup

Figure 3.18 shows the set up for the microfluidic tests. Once the reservoir is filled with a certain liquid using a micropipette, the liquid will start flowing through the channel, if the liquid is affected by enough surface tension force. A high resolution CCD camera records the liquid flow in the channels during the experiment. Three different liquids including water, glycerine, and ethanol will be tested in the experiments. A fluorescent dye and UV black light are used to visualize the liquid flow, because the liquids are achromatic, making observation without fluorescent dye difficult. Only tiny volume of the fluorescent dye is mixed with the target liquids to prevent the material properties of the liquids from changing. For all cases, the fluorescent dye (50µl) was mixed with the base liquid (3ml) so that the concentration of fluorescent dye is less than 2% of the total volume of liquid. Thus the fluorescent dye gives a minor effect on the material properties. The reservoirs on polyethylene and PMMA were filled with 20µl of each liquid, and only 0.5µl of liquid was filled into the reservoir on silicon.
To apply different surface tension force during the liquid flow, materials were selected with a different contact angle, a surface tension coefficient and a viscosity coefficient. Among test materials, water and glycerine have a relatively high surface tension and a high contact angle on various solid surfaces. Meanwhile, ethanol has relatively low surface tension and a low contact angle. A wetting distance is the distance that a liquid droplet travels on a solid surface by diffusion resulting only from the surface tension. A low contact angle generally creates a long wetting distance. Conversely, a high contact angle allow liquid to travel to a limited distance. Thus, when the contact angle is 0°, liquid can theoretically travel an unlimited distance on a free surface. Viscosity is another
important factor allowing the liquid flow in a microchannel. Materials with high viscosity may not flow through a microchannel, because shear stress, generated as a result of viscosity, disturbs liquid movement.

### 3.3.3 Experiment results

Table 3.2 shows the material properties of three materials for the liquid flow test. Glycerine has a high viscosity, approximately 1000 times larger than the other two materials. Water and glycerine have the similar surface tension, and water and ethanol have approximately the same viscosity when compared to glycerine. However, the surface tension of water is approximately three times larger than that of ethanol.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (kg/m$^3$)</th>
<th>Surface tension (mN/m)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>998</td>
<td>72.8</td>
<td>1.002</td>
</tr>
<tr>
<td>Glycerine</td>
<td>1261</td>
<td>63</td>
<td>1490</td>
</tr>
<tr>
<td>Ethanol</td>
<td>789</td>
<td>22.27</td>
<td>1.200</td>
</tr>
</tbody>
</table>

After setting up the experiment, the liquid materials were filled into the reservoir of each microchannel system. Figure 3.19 shows the front of liquid flow in the channel, observed through optical microscope and Figure 3.20 demonstrates the microchannels after the liquid flow has completely arrived at the end of the channel. During the experiment, no overflow was observed around polymers channels. However, the overflow happens
around the reservoir on silicon due to the shallow reservoir. For the measurement of liquid behavior, only velocity was measured in the length direction (x direction) due to the limited experiment.

Figure 3.19 The front of liquid flow in the channel of polyethylene
Results revealed that the microchannels machined by the excimer laser process are suitable for the liquid flow on all three materials that were tested. Figures 3.21 through 3.23 demonstrate the distance of liquid flow. It indicated that all liquid reached the end of channels but with different flow duration (different mean velocity). Figures 3.24 through 3.26 represent the velocity of three liquids in the length direction on the different microchannels. To measure the velocity, the travel distance of liquid was measured at every 100ms and the velocity of liquid flow was calculated based on the distance measurement and the time interval. In the experiment, Ethanol represented the highest velocity regardless of the material of microchannel. Glycerine showed the lowest velocity among the three liquids, probably due to the high viscosity of glycerine. The velocity of glycerine maintains, comparatively, a constant value throughout the liquid flow, as described in from Figures 3.24 to 3.26. Although a low velocity was observed during the experiment, it reached the end of the channel with continuous movement. The
velocity of Ethanol and water, on the other hand, decreased as liquid flowed through the channel, and oscillated within a certain range. The range of velocity oscillation decreased as the liquid continued to flow. Figures 3.24 through 3.26 can be explained clearly by reference to Equation (3.10). The velocity of all liquids decreases as the liquid travels toward the end of the channel. On the velocity graph, the liquid velocity suddenly changes. It is due to the measurement error or non-continuous surface tension force in the channels. As mentioned before, liquid with high viscosity, such as glycerine, shows a very low velocity. Water has a lower viscosity and higher surface tension compared to Ethanol. However, the velocity of water is smaller than the velocity of ethanol, probably due to the different contact angle between the two liquids. The contact angle of ethanol may be much lower than the contact angle of water.

Figure 3.21 Travel distance of liquid flow in the microchannel of polyethylene
Figure 3.22 Travel distance of liquid flow in the microchannel of PMMA

Figure 3.23 Distance of liquid flow in the microchannel of silicon
Figure 3.24 Velocity of liquid flow in the channel of polyethylene

Figure 3.25 Velocity of liquid flow in the channel of PMMA
3.4 Summary

In this chapter, excimer laser micromachining and the liquid flow through microchannels created by excimer laser micromachining were discussed. Excimer laser micromachining could generate microchannels much easier than other nano/micro fabrication methods, because it simply uses a tool path to create structures without any masking process. Furthermore, parametric study of laser micromachining is necessary to create more accurate structures. After fabrication of the microchannels, microfluidic experiments were performed to verify the liquid flow through the channels. Three different liquids along with fluorescent dye were used to visualize the liquid flow. The
results showed that all three liquids could be allowed to flow through the microchannel, regardless of viscosity or surface tension. Only different velocity in different materials was observed. It is also observed that higher viscosity resulted in a lower velocity in the microchannel. In addition, the velocity of liquid flow in all cases gradually decreased over time. In this research, it was revealed that laser micromachining is a good candidate to fabricate a microchannel system with several advantages compared to other fabrication methods.
CHAPTER 4
A GEOMETRIC METHOD TO ANALYSE THE CONTACT ANGLE FOR MICROCHANNELS DESIGN

In this chapter, a geometric analysis and modelling method are presented to calculate the contact angle of microfluidic liquid on the solid substrate to apply for micro bio-device development. To estimate the contact angle of microfluidic, it is assumed that liquid spreads out ideally based on the liquid surface tension and other forces, so it diffuses at equal distances in all directions. Based on this assumption, the geometry of a droplet is analyzed and the wetting distance is derived as the function of liquid volume, a contact angle and material properties. In the study, two models are developed: one for large droplets and another for very tiny droplets. The large droplet considered gravitational effects in terms of material properties. To validate the estimated contact angle, a certain volume of liquid was dropped on the solid substrate, and then the wetting distance of the liquid droplet is measured. The measured wetting distance was compared with the theoretical wetting distance calculated by the analytical models. For comparison, different materials were used in experiments with goniometer for validation. The presented techniques can be used for the design and selection of machining parameters for the micro bio-devices development.
4.1 Introduction

A contact angle is the angle that the liquid droplet makes an angle with solid, gas or another liquid interface. It is caused by the different tension forces among the gas/liquid, liquid/solid and gas/solid interface. There are basically two types of contact angles, which are a static contact angle and a dynamic contact angle (advancing and receding contact angles). The static contact angle is the angle observed when the liquid is in the equilibrium status after completely spreading. On the other hand, the dynamic contact angle is the contact angle observed while the liquid maintains movement, so it varies over time. Figure 4.1 shows the contact angle of water on polyethylene. The wetting phenomenon is an important issue in various technological processes [Hartland 2004]. It relies on material properties, including surface tension and the contact angle. Once liquid comes into contact with a solid surface, it starts to diffuse on the solid surface with intermolecular interactions, whereas surface tension tends to minimize the surface area of the droplet. The wetting can simply explain using in terms of a contact angle. If the contact angle approaches 0° (hydrophilic), the liquid completely spreads out (complete wetting), and the angle that is larger than 90° (hydrophobic) means that the liquid spreads in only a small distance (incomplete wetting). It is also a good indicator to explain the microfluidic phenomenon in microchannels. Generally, the contact angle can be a boundary condition in the microchannel during the liquid flow. It is somewhat difficult to explain the liquid behavior with only a contact angle. However, it still provides good prediction for liquid behavior.
The contact angle is measured when solid/liquid, solid/gas and liquid/gas interface tension forces—(respectively, $\gamma_{sl}$, $\gamma_{sg}$ and $\gamma_{lg}$) —meet at the equilibrium condition, as shown in Figure 4.2. The contact angle can be calculated using those three tension forces.

The summation of tension forces in the horizontal direction should be zero at equilibrium. Finally, the contact angle can be represented by Equation (4.1). If the tension forces for all interfaces are known, the contact angle can be easily calculated. However, it is difficult to determine the tension forces.
Generally, there are two frequently used methods—the sessile drop method and the Wilhelmy method—to measure a contact angle. The sessile drop method can measure the contact angle using goniometer, consisting of a high resolution camera and imagining software, to capture and analyze a liquid droplet. Once a liquid droplet is deposited on the solid surface, the image of the side view of the droplet is captured, and the contact angle measured. However, it is still hard to define the contact line on the solid surface and to assign the tangent line on the droplet [Goclawski 2007]. Whilemy method uses tensiometry, consisting of a sensitive force meter. The sensitive force meter, which has a probe with a uniform geometry is dipped into (for an advancing contact angle) or withdrawn from (for a receding contact angle) test liquid source to measure a force. After measuring the force, a contact angle can be calculated, using the force, surface tension and the probe geometry. Behind the two major methods, several other methods have been introduced. Some studies employed the wetting area of a droplet to calculate a contact angle, but they did not consider gravitational effects [Njobuenwu 2007]. Current methods included the sessile drop method and the Wilhelmy method can provide somewhat accurate results. However, it is necessary to access equipment to measure contact angles with the methods. Furthermore, it is difficult to measure the contact angles for certain liquids due to their rapid evaporation or very small contact angles, and it is also still a
critical issue to define tangent line especially, when the boundary of droplet is not clear as mention before. Thus, other methods of measuring contact angles are required.

In this chapter, the method to calculate a contact angle is proposed. In order to determine the contact angle using this method, experiments involving a few different liquids and substrates were conducted, and the measured wetting distances are compared to the theoretical wetting distance calculated by the model to evaluate contact angles. Furthermore, the contact angles are measured by the goniometer to confirm the method. This method can replace the current method. Furthermore, it can be used to design microarray and microfluidic devices.

4.2 Design evaluation of microfluidic devices

To develop the micro bio-devices, an appropriate fabrication process should be developed. However, the design of system (system functionality) cannot evaluate with fabrication process. The design of micro bio-device such as microfluidic systems and microarrays should be determined using the proposed method based on materials of the systems and applied materials (generally, liquid-based materials) before fabrication. Once materials and designs are decided, the design can be determined by predictive methods. Many bio-devices such as LOC (lab-on-a-chip) are related to liquid flow on the system [Haeberle 2007]. A contact angle is negligible in bulk size. However, when the system is in a small scale, including micro- and nano- scale, the contact angle is one of major influential factors. The contact angle explains the diffusion of liquid droplet on the flat surface as well as the liquid flow in the microchannels [Lee 2010]. Figure 4.3 describes
the development stage of micro bio-devices. Virtual estimation of designs can dramatically reduce the development time. Virtual estimate can be achieved by analytical modeling or simulation method. The optimized design is created by the different process control of microfabrication methods and the process parameters should be evaluated by virtual estimation of design before fabrication. In general, the dynamic contact angle instead of the static contact angle should be given for more accurate results. However, it is hard to estimate the dynamic contact angle because it varies according to liquid flow. Additionally, it is reported that the results between using the dynamic and the static contact angle does not show meaningful differences [Saha 2009].

Figure 4.3 Virtual estimation of design with a contact angle
4.3 **Theoretical study of determination of a contact angle**

The geometry of the liquid droplet is simplified to construct a mathematical model. Many researchers have attempted to build a math model for the liquid drop, assuming that the droplet is an ideal sphere [Baikov 2003, Alteraifi 2003]. In this research, a different approach related to the geometry of the liquid droplet is employed to build the model. The math models were derived in order to calculate a contact angle based on the wetting distance, the volume of the liquid droplet and material properties. In general, the wetting distance of a liquid droplet is primarily dependent upon the contact angle. A small contact angle allows the liquid to spread over long distances. Meanwhile, the liquid with a large contact angle spreads over a short distance. Additionally, a large volume of liquid travels a longer distance as shown in Figure 4.4.

![Figure 4.4 Liquid droplet according to different contact angles: a>b>c](image)

However, if a large volume of liquid is dropped on the surface, gravity is not negligible any more. Thus, the top surface of a droplet forms a flat surface, instead of a circular shape, as shown in Figure 4.5 (b). Other factor such as surface roughness may change the shape of droplet. However, in the study, it is assumed that the solid surface has fine surface roughness.
Now, it must be known how to determine large and small volumes. The gravity effect on the liquid droplet on the solid surface can be explained by a capillary length ($\kappa^{-1}$), shown as the following equation [De Gennes 2004].

$$\kappa^{-1} = \sqrt{\frac{\gamma}{\rho g}}$$ \quad (4.2)

$\gamma$, $\rho$ and $g$ indicate the surface tension of the gas/liquid interface, the density of liquid and gravity acceleration, respectively. If the capillary length is much smaller than half of the wetting distance, the effect of gravity dominates the liquid droplet; this means that the droplet has a large flat surface on top. Conversely, when it is much higher than half of the wetting distance, gravity is negligible. In this chapter, two geometrical models will be derived to explain the gravity effect. For the small volume, only the droplet shape is considered, but the effect of gravity is included for the large droplet. Table 4.1 shows the material properties and capillary lengths of a few materials.
Table 4.1 Material properties and capillary lengths

<table>
<thead>
<tr>
<th></th>
<th>Acetone</th>
<th>Water</th>
<th>Glycerine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Tension (mN/m)</td>
<td>23.7</td>
<td>71.97</td>
<td>63</td>
</tr>
<tr>
<td>Density (kg/m3)</td>
<td>790</td>
<td>998</td>
<td>1261</td>
</tr>
<tr>
<td>Capillary length (mm)</td>
<td>1.75</td>
<td>2.71</td>
<td>2.26</td>
</tr>
</tbody>
</table>

4.3.1 Model I: Math model for a small droplet

The liquid droplet can be simplified for a tiny volume, as shown in Figure 4.6. It assumes that the droplet forms a perfect sphere on the solid surface because the gravity effect is negligible. The liquid droplet is part of a complete sphere. Now, the radius of the sphere (R), the distance from the center of the sphere to the solid surface (H) and the thickness of the droplet (h) can be expressed using the contact angle (θ) and the wetting distance (W). Equations (4.3) through (4.5) represent R, H and h as the function of a wetting distance and a contact angle.

\[
R = \frac{W}{\sin \theta} \quad (4.3)
\]

\[
H = \frac{W}{\tan \theta} \quad (4.4)
\]

\[
h = R - H = W \left( \frac{1}{\sin \theta} - \frac{1}{\tan \theta} \right) \quad (4.5)
\]
With the assumptions and a certain liquid volume, the wetting distance can be calculated. And then the calculated wetting distance can be compared with a real wetting distance, obtained from experiments. A droplet is expressed as Equation (4.6).

\[ x^2 + y^2 + (z + H)^2 = R^2 \]  

(4.6)

Based on the sphere model, the liquid volume can be calculated using the droplet shape shown, as follows.

\[ z = \sqrt{R^2 - x^2 - y^2} - H \]  

(4.7)

\[ V = \iint_D \sqrt{R^2 - x^2 - y^2} - H \, dA \]  

(4.8)
After solving Equation (4.9),

$$V = \int_{0}^{2\pi} \int_{0}^{W} (\sqrt{R^2 - r^2} - H) r dr d\theta \quad W \in (0, R) \quad (4.9)$$

Substituting Equations (4.3) and (4.4) into Equation (4.10), the wetting distance is expressed as Equation 4.11.

$$V = \frac{2}{3} \pi \left( R^3 - H^3 - \frac{3}{2} HW^2 \right) \quad (4.10)$$

$$W = \frac{\sqrt{3V \sin^3 \theta \tan^3 \theta}}{\pi (2 \tan^3 \theta - 3 \sin^3 \theta \tan^2 \theta - 2 \sin^3 \theta)} \quad (4.11)$$

Thus, the total wetting distance is

$$D = 2W = \frac{\sqrt{3V \sin^3 \theta \tan^3 \theta}}{\pi (2 \tan^3 \theta - 3 \sin^3 \theta \tan^2 \theta - 2 \sin^3 \theta)} \quad (4.12)$$

### 4.3.2 Model II: Math model for a large droplet

A large volume of a droplet can be simplified, as shown in Figure 4.7. The top surface maintains a constant thickness, and the side of the droplet shows a circular shape.
As shows in Figure 4.1 (b), large volume droplet does not form a perfect flat top surface. However, as volume increases, the top surface approaches a flat surface.

The study starts from the thickness of the liquid droplet. A well-known equation, as follows, expresses the thickness of the droplet on a certain substrate [De Gennes 2004].

$$h = \sqrt{\frac{2\gamma(1 - \cos\theta)}{g\rho}}$$

(4.13)

$\gamma$, $\theta$, $g$ and $\rho$ indicate surface tension between air and liquid, a contact angle, gravity acceleration and liquid density, respectively. It is the maximum thickness of a droplet
with a given contact angle under the effect of gravity. If the surface tension is known, the thickness of the droplet is the function of a contact angle. R and R’ from Figure 4.6 can also be represented by a contact angle, as follows.

\[
R = \frac{h}{1 - \cos \theta} = \frac{\sqrt{2y}}{\sqrt{\gamma \rho (1 - \cos \theta)}} \quad (4.14)
\]

\[
R' = \frac{h \sin \theta}{1 - \cos \theta} = \frac{\sqrt{2y \sin \theta}}{\sqrt{\gamma \rho (1 - \cos \theta)}} \quad (4.15)
\]

A liquid volume for a large droplet is explained by the following equations.

\[
V = \pi \int_{R-h}^{R} x^2 \, dz \quad (4.16)
\]

\[
V = \pi \int_{R-h}^{R} \left( d^2 + R^2 - z^2 + 2d\sqrt{R^2 - z^2} \right) \, dz \quad (4.17)
\]

Equation (4.17) can be represented by Equation (4.18) after solving the integral.

\[
V = \pi \left[ d^2 h + Rh^2 - \frac{1}{3} h^3 + d \left[ -(R - h)\sqrt{2Rh - h^2} + R^2 \left( \frac{\pi}{2} - \sin^{-1} \frac{R-h}{R} \right) \right] \right] \quad (4.18)
\]

In Equation (4.18), the first term on the right side indicates the volume of the top part of the droplet, and the remaining terms on the right side express the volume of the sides of the droplet. Using Equation (4.18), the radius of the top flat area (d) can be calculated as the following equation.
Equation (4.19) can be rearranged by substituting Equation (4.13) and (4.14) into (4.19). Thus, the radius of the top circle (d) would be expressed by material properties, the contact angle and the volume of the liquid.

\[
d = \frac{\cos \theta}{1 - \cos \theta} \sqrt{\frac{\gamma(1 + \cos \theta)}{2 gp}} - \frac{1}{1 - \cos \theta} \sqrt{\frac{\gamma}{2 gp(1 - \cos \theta)}} \left(\frac{\pi}{2} - \sin^{-1}\cos \theta\right) + \frac{2 \cos \theta}{1 - \cos \theta} \sqrt{\frac{\gamma(1 + \cos \theta)}{2 gp}} - \frac{1}{1 - \cos \theta} \sqrt{\frac{\gamma}{2 gp(1 - \cos \theta)}} \left(\frac{\pi}{2} - \sin^{-1}\cos \theta\right)
\]

The wetting distance is expressed with the summation of the diameter of the inside circle (2d) and the diameter of the side circle (2R').

\[
D \text{ (wetting distance)} = 2d + 2R'
\]

Thus, the final equation for wetting distance through the expression of material properties, the contact angle and the liquid volume is as indicated below.

\[
D = \frac{2 \cos \theta}{1 - \cos \theta} \sqrt{\frac{\gamma(1 + \cos \theta)}{2 gp}} - \frac{1}{1 - \cos \theta} \sqrt{\frac{\gamma}{2 gp(1 - \cos \theta)}} \left(\frac{\pi}{2} - \sin^{-1}\cos \theta\right) + \frac{2 \cos \theta}{1 - \cos \theta} \sqrt{\frac{\gamma(1 + \cos \theta)}{2 gp}} - \frac{1}{1 - \cos \theta} \sqrt{\frac{\gamma}{2 gp(1 - \cos \theta)}} \left(\frac{\pi}{2} - \sin^{-1}\cos \theta\right)
\]

\[
(4.22)
\]
Now, Equation (4.22) simply relies on material properties (surface tension and density), gravity, the contact angle and the liquid volume. Thus, the wetting distance can be calculated with determined the liquid volume, contact angle and material properties. This model assumes that thickness is the function of a contact angle and material properties, instead of geometrical factors, as assumed by the previous model. This means that a sufficiently large liquid volume must be used to satisfy the thickness. The minimum required volume is the value when \( d \) in Figure 4.7 is zero. Two models have the same wetting distance exactly at the minimum required volume. The minimum required volume for Model II can be derived from Equation (4.18), shown as Equation (4.23).

![Figure 4.8 Volume required according to a contact angle](image)

If the volume exceeds the value calculated by Equation (4.23) at the given contact angle, \( W \) is not zero and the flat top surface will be formed. Figure 4.8 plots the minimum required volume with three different liquids.
\[ V_{\text{required}} = \frac{2\pi\gamma(2 + \cos\theta)\sqrt{2\gamma(1 - \cos\theta)}}{3\gamma \rho \sqrt[3]{\gamma \rho}} \]  

(4.23)

Equation (4.23) can be represented with the capillary length, shown as Equation (4.24). When even the capillary length is larger than half of the wetting distance, but the given liquid volume is less than the required volume calculated by Equation (4.24), the first model instead of the second model must be used for more accurate results.

\[ V_{\text{required}} = \frac{2\sqrt{2}\pi(2 + \cos\theta)\sqrt{(1 - \cos\theta)}}{3(\kappa^{-1})^3} \]  

(4.24)

### 4.4 Numerical method to solve the mathematical models

Equations (4.12) and (4.22) can be used to find the contact angles and the wet distance of droplets for microfluidic design. However, given the number of variables in Equations (4.12) and (4.22), it is difficult to solve both equations. Even though the volume \( V \) and the wetting distance \( D \) are known, the contact angle \( \theta \) may not be easily found by a simple calculation. In this chapter, a numerical method is developed to solve Equations (4.12) and Equation (4.22) to determine the correct microfluidic contact angle. Fig. 9 shows the flow chart of the numerical method to solve the governing equations (4.12) and (4.22) of Models I and II. As shown in Figure 4.9, the liquid droplet volume \( V \) and the measured wetting distance \( D_{\text{mea}} \) are first input. The measured wetting distance \( D_{\text{mea}} \) is compared with the capillary length \( \kappa \) to determine either to use Model I or Model
II. Once a correct model is selected, the search for the correct contact angle $\theta$ starts by calculating the analytical wetting distance $D$. In this chapter, an iterative search algorithm is used to locate the correct contact angle $\theta$. As shown in Fig. 4.9, with the given liquid volume $V$ and the current searching angle $\theta_i$, the analytical wetting distance $D_i$ is calculated by using Equations (4.12) and (4.22). The calculated $D_i$ is compared with the measured wetting distance $D_{\text{mea}}$. If the error of $|D_i - D_{\text{mea}}|$ is larger than a predefined tolerance $\tau$, a new search angle $\theta_{i+1}$ is adjusted from the current angle $\theta_i$ by an adjustment search step $\Delta \theta_i$ shown as follows:

$$
\theta_{i+1} = \theta_i \pm \Delta \theta_i, \quad \text{IF } |D_i - D_{\text{mea}}| > \tau
$$

(4.25)

In Equation (4.25), the + or − adjustment direction is determined by either the calculated $D_i$ is smaller or larger than the targeted $D_{\text{mea}}$. The iterative searching process will stop, when the calculated wetting distance $D_i$ falls within the acceptable range of the targeted $D_{\text{mea}}$, i.e., $|D_i - D_{\text{mea}}| < \tau$. Once the termination condition is satisfied, the final contact angle $\theta_{\text{final}}$ is calculated by a linear interpolation between the last two searching points $(D_i, \theta_i)$ and $(D_{i-1}, \theta_{i-1})$, shown as follows:

$$
\begin{align*}
\theta_{\text{final}} &= \theta_i & \text{if } D_{\text{mea}} = (D)_i \\
\theta_{\text{final}} &= \frac{\theta_i - \theta_{i-1}}{(D)_i - (D)_{i-1}}(D_{\text{mea}} - (D)_i) + \theta_i & \text{if } D_{\text{mea}} > (D)_i
\end{align*}
$$

(4.26)

Figure. 4.9 describes the flow chart of the discussed iterative numerical method.
Start

Calculate a theoretical wetting distance ($D_i$)

Input the liquid volume ($V$)
Input the wetting distance ($D_{mea}$)
Input material properties ($\rho$, $\gamma$ and $\kappa^{-1}$)

$D_{mea}/2 < \kappa^{-1}$

Model I
Calculate a theoretical wetting distance ($D_i$)

$D_i < = D_{mea}$

Calculate the contact angle by linear interpolation

Model II
Calculate a theoretical wetting distance ($D_i$)

$D_i < = D_{mea}$

Calculate the contact angle by linear interpolation

$V > = V_{required}$

End

Figure 4.9 Flow chart of the numerical method to determine a contact angle
4.5 Measurement of a wetting distance with given liquid volume

4.5.1 Setup to measure a wetting distance

First of all, after dropping the given liquid volume by a micropipette, the wetting distance was measured and used to compare with the theoretical wetting distance calculated by the model. Three different solid surfaces—silicon, glass and polyethylene—were used as substrates, and water, glycerine and acetone were used to measure the contact angles. In general, it is well known that acetone has a very small contact angle on various materials. On the other hand, water and glycerine have a relatively high contact angle on many solid surfaces. In this study only static contact angle instead of a dynamic contact angle (advancing and receding) is considered. Thus, certain amounts of time must be allowed while the wetting is completed. The measurement of the wetting distance was performed after the liquid completely spreads over the substrate. Three different volumes are used to measure the wetting distance in order to determine whether the different volume results in any effect on the contact angle. The contact angle on each different volume should have the same value for the same liquid on the same substrate. The easiest way to measure the wetting distance is using a top view of the droplet. However, when the wetting distance is measured, there are two possible cases, as shown in Figure 4.10. If the contact angle is smaller than 90°, the wetting distance can be measured using the top view. On the other hand, when the angle is larger than 90°, the distance measured with the top (D’ in Figure 4.10) view is no longer a true wetting distance. When the contact angle is 100°, the difference between D’ and D in Figure 4.10 is approximately
9%, regardless of the liquid volume. However, if the contact angle is much larger than 90° and D is used to measure the contact angle, it will seriously impact the final result. In the experiment, most liquids are hydrophilic on the surface, so the contact angle over 90° is not considered in the model.

![Diagram of liquid droplet](image)

Figure 4.10 Liquid droplet on the substrate: (a) contact angle <90°, (b) contact angle > 90°

For stable measurement, the pictures of the top view of a droplet were taken, as indicated in Figure 4.11. The wetting distance was measured by ImageJ software (image processing software). The experiments were conducted in ambient conditions (temperature 22°C and humidity 24.5%). Silicon (100) and glass substrates were cleaned with acetone and methanol in an ultrasonic bath, and polyethylene were cleaned by methanol. All substrates were dried for sufficient amounts of time in order to maintain a completely dry surface.
4.5.2 Results and discussion

4.5.2.1 Contact angle measured using the math model

Different volumes of liquid (1, 5 and 10\textmu l) were used for the experiment. Table 4.2 shows the results of the measurements of wetting distances, according to given liquid volumes. Based on the measured wetting distances in Table 4.2, contact angles were calculated, as shown in Table 4.3. Contact angles maintain relatively constant values, regardless of the droplet volume for the same liquids on the same substrates. However, in some cases, the contact angle increases as the liquid volume increase. For example, in most cases involving acetone, the contact angle slightly increased, regardless of what type of substrate was used, when a larger liquid volume was utilized to measure the contact angle. This is probably due to the evaporation that occurs during the wetting process. In general, acetone evaporates very rapidly, and evaporation is a function of the
surface area of liquid exposed to air. A large volume usually spread the liquid out further, and evaporation occurs more quickly. Acetone might be evaporated before the wetting is completely finished. Evaporation may not be important for other cases, including water and glycerine. Results involving water and glycerine do not align with the trends indicated by acetone. The contact angle is varied within a certain range, from 0° to 10°, for most cases. This may be explained by measurement errors, or the fact that the liquid did not form a perfect sphere. In cases of larger contact angles, small measurement errors can make a serious difference. Thus, one important factor for obtaining an accurate result is to measure the wetting distance accurately.
Table 4.2 Measured wetting distances from the experiment

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Water (mm)</th>
<th></th>
<th>Glycerine (mm)</th>
<th></th>
<th>Acetone (mm)</th>
<th></th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>10µl</td>
<td>1µl</td>
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</tr>
<tr>
<td>Silicon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>2.6</td>
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<td>0.071</td>
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</tr>
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<td>0.071</td>
<td>0.045</td>
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<td>0.089</td>
</tr>
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</table>
Table 4.3 Contact angles calculated by the math models based on Table 4.2

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Water (degree)</th>
<th>Glycerine (degree)</th>
<th>Acetone (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1µl</td>
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<td>10µl</td>
</tr>
<tr>
<td>Silicon</td>
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</tr>
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<td>32.9</td>
</tr>
<tr>
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<td>31.6</td>
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<td>31.4</td>
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<tr>
<td>AVG</td>
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<td>32.4</td>
</tr>
<tr>
<td>Error(RMS)</td>
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<td>30.9</td>
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<td>30.0</td>
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<tr>
<td>AVG</td>
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<td>62.0</td>
<td>63.0</td>
</tr>
<tr>
<td>Error(RMS)</td>
<td>7.34</td>
<td>8.19</td>
<td>6.98</td>
</tr>
</tbody>
</table>
4.5.2.2 Contact angle measured using sessile drop method

In order to verify the proposed method, contact angles were measured using goniometer. The measurement of contact angles for acetone was not performed because it generally shows very low contact angles, regardless of the solid surface, so it is difficult to obtain the image due to the thin thickness of the droplet. SEO phoenix 150 manual type contact angle analyzer was used for experiment. After obtaining high resolution images, the contact angles were estimated by ImageXP software. ImageXP draws the base line and the tangent line on the liquid droplet automatically. Figure 4.12 shows the droplet images taken by goniometer. The contact angles of water and glycerine were measured on silicon, glass and polyethylene. Table 4.4 indicates the contact angles measured by the equipment.

![Droplet images to measure contact angles](image)

Figure 4.12 Droplet images to measure contact angles
Table 4.4 The contact angles measured with goniometer

<table>
<thead>
<tr>
<th></th>
<th>Silicon</th>
<th>Glass</th>
<th>Polyethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>30.2°</td>
<td>32.7°</td>
<td>69.7°</td>
</tr>
<tr>
<td>Glycerine</td>
<td>45°</td>
<td>51.9°</td>
<td>67.2°</td>
</tr>
</tbody>
</table>

### 4.5.2.3 Comparison of results between the geometrical model and sessile drop method

Figure 4.13 represents the wetting distance according to the contact angle based on the model. The wetting distance dramatically increases at the contact angle below 10°, but it is not significantly different at contact angles over 10°, regardless of liquid volume. This indicates that the measurement of a wetting distance is very critical, especially when the contact angle exceeds 10°. In such cases, small measurement errors of the wetting distance will significantly alter the corresponding contact angle.

![Figure 4.13 Relationship between the contact angle and wetting distance](image-url)
Figures 4.14 and 4.15 compare the contact angles between the model and sessile drop method. The purple dotted line on each graph indicates the contact angle measured by the goniometer. There is up to 13% difference between the two results.
Figure 4.14 Comparison of contact angles for water between the proposed method and using goniometer: from top to bottom, contact angle of water on silicon, glass and polyethylene
Figure 4.15 Comparison of contact angles for glycerine between the proposed method and using goniometer. From top to bottom, contact angle of glycerine on silicon, glass and polyethylene.
4.5.2.4 Difference between Model I and Model II

Now, the discussion moves to the difference between Model I and Model II. Model II cannot be used when the volume is less than the required volume, whereas, Model I can also be applied for the larger volumes. However, the result would be different, as indicated in Figure 4.16. Model I reduces the real contact angle because it does not consider the gravity effect.

Figure 4.16 Description of difference between Model I and Model II

To compare the results between the two models, the contact angles was calculated with a given wetting distance, and 120µl of water (Table 4.5). Model II shows higher contact angles in all cases. Difference between the two models is larger at lower contact angles.

Table 4.5 The contact angle calculated by Model I and Model II (water volume: 120µl)

<table>
<thead>
<tr>
<th>Wetting distance (mm)</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
<th>22</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model I (°)</td>
<td>85.7</td>
<td>58</td>
<td>37.6</td>
<td>24.7</td>
<td>16.8</td>
<td>12</td>
<td>8.7</td>
<td>6.6</td>
<td>5.1</td>
</tr>
<tr>
<td>Model II (°)</td>
<td>85.9</td>
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<td>39.8</td>
<td>27.7</td>
<td>20</td>
<td>15.1</td>
<td>11.7</td>
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<tr>
<td>Δ degree</td>
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<tr>
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</tbody>
</table>
Furthermore, the difference between two models may be more significant at larger volumes. To verify that, the contact angle of water was estimated on polyethylene with large volumes (500µl and 1000µl), as shown in Table 4.6. As the liquid volume increases, the error of Model I increases, whereas the error of Model II decreases. Thus, the difference between two models increases as the liquid volume increases. The error measured was based on the contact angle of water (69.7°) indicated in Table 4.4.

Table 4.6 Contact angle of water measuring by large volume

<table>
<thead>
<tr>
<th>500µl water</th>
<th>wetting distance (mm)</th>
<th>contact angle (°)</th>
<th>error of contact angle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Model I</td>
<td>Model II</td>
</tr>
<tr>
<td>1</td>
<td>15.9</td>
<td>59.6</td>
<td>75.9</td>
</tr>
<tr>
<td>2</td>
<td>15.6</td>
<td>62.0</td>
<td>77.0</td>
</tr>
<tr>
<td>3</td>
<td>16.1</td>
<td>58.2</td>
<td>74.3</td>
</tr>
<tr>
<td>4</td>
<td>15.9</td>
<td>59.3</td>
<td>75.6</td>
</tr>
<tr>
<td>5</td>
<td>15.9</td>
<td>59.7</td>
<td>76.1</td>
</tr>
<tr>
<td>Avg</td>
<td>15.9</td>
<td>59.8</td>
<td>75.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1000µl water</th>
<th>wetting distance (mm)</th>
<th>contact angle (°)</th>
<th>error of a contact angle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Model I</td>
<td>Model II</td>
</tr>
<tr>
<td>1</td>
<td>23.3</td>
<td>41.8</td>
<td>65.2</td>
</tr>
<tr>
<td>2</td>
<td>23.2</td>
<td>42.4</td>
<td>66.0</td>
</tr>
<tr>
<td>3</td>
<td>22.5</td>
<td>45.6</td>
<td>70.0</td>
</tr>
<tr>
<td>4</td>
<td>23.2</td>
<td>42.7</td>
<td>66.3</td>
</tr>
<tr>
<td>5</td>
<td>22.7</td>
<td>44.6</td>
<td>68.8</td>
</tr>
<tr>
<td>Avg</td>
<td>23.0</td>
<td>43.4</td>
<td>67.3</td>
</tr>
</tbody>
</table>
4.5.2.5 Microarray design using the proposed method

So far, the method to measure contact angles has been discussed. However, it can be used for estimation and design of micro systems. As an example, when microarray is designed, the size of array and the distance between neighbors should be addressed. For the case, the size of microarray can be estimated by the proposed models. Figure 4.17 describes the microarray. In generally, there are several different methods to create microarrays. Some methods do not need to estimate the dimension presented in Figure 4.17 due to physical isolation. However, other methods such as using a material print should find out the critical dimension before creating the microarray. The method can estimate the wetting distance with a given liquid volume during design the microarray. So, if the area and other conditions are given, estimation of the size of microarray is required. Conversely, if the size of array and other conditions are given, the required area can be estimated.

Figure 4.17 The design of microarray for medical purposes
4.6 Summary

In this chapter, the analytical model was developed based on the simplified geometry in order to measure a contact angle. Models for two different cases—a small droplet (Model I) and a large droplet (Model II)—were derived with and without the gravity effect. The proposed method uses a math model based on the liquid volume, the wetting distance and material properties. It is a good approximation method to measure the contact angle without any equipment. The results show that the contact angle of the same liquid on the same substrate maintains approximately the same value, regardless of the liquid volume. In order to verify the model contact angles were measured with goniometer and the results were compared. It revealed that the model is accurate, within ±13% compared to the real contact angle. In general, the difference in contact angles of the same liquid is due to various factors, including the evaporation of the liquid, measurement errors of the wetting distance during experiments, and geometrical errors. Model II cannot be used for a tiny droplet because it needs the minimum required volume to form a theoretical thickness. However, Model I can be used for a large volume, but the results may not be correct because the assumption of Model I is not valid for a large volume. Furthermore, both models were tested for large volumes of water. Results revealed that Model II provided less error than Model I. The original purpose of this research is to build the method models to estimate the contact angle without equipment. However, it can be used to design and estimate microarrays and microfluidic systems.
CHAPTER 5

GEOMETRICAL EFFECTS ON LIQUID BEHAVIOR IN MICROCHANNELS AND THE RELATIONSHIP BETWEEN CHANNEL GEOMETRY AND LASER PARAMETERS

The present study focuses on the geometrical effects of liquid behavior in microchannels created by excimer laser micromachining and the relationship between channel geometry and laser parameters. In this research, the effect of different widths and depths of a microchannel (a different aspect ratio or a different hydraulic radius) is examined through experiment and simulation. Furthermore, the liquid profile in microchannels was evaluated based on contact angles. Five different microchannels were fabricated with different aspect ratios and hydraulic radii. Microfluidic experiments were conducted to determine the liquid velocity in the length direction of microchannels, as discussed in Chapter 3. In addition, simulation was performed using Ansys Fluent to confirm the experimental results. In the last part, the relationship between the design of the microchannel in terms of functionality (microfluidic) and laser parameters are derived. The results can be used to optimally design and fabricate microfluidic systems.
5.1 Introduction

All microsystems have their own functionalities. It is important to evaluate those functionalities with the proper methods. The objective of this research is to apply Excimer laser micromachining to microfluidic systems such as bio-medical devices. Thus, the functionality should be evaluated with liquid flow [Kim 2010b]. For liquid flow, there are three influential factors. The most important factor is the force applied, including surface tension, pressure and centrifugal force, that allows the liquid to flow through microchannels. Another important factor is the geometry of the microchannel, because different geometries, such as depth, width and profile of a channel influence the liquid flow. Material properties such as viscosity and density also affect the liquid flow.

The effect of different widths of a microchannel on the pressure-driven flow was examined by experiment and simulation [Kim 2002]. These revealed that larger widths of microchannels support better developed liquid flows. On the other hand, Chen et al. [Chen 2008] examined the effect of both the width and depth of a microchannel. In this study, only surface tension was the dominant force for developing liquid flows. Better developed liquid flow was observed in the channel with a higher aspect ratio (depth/width). Dutta et al. (2006) examined the effect of channel geometry on a pressure-driven microfluidic system. They compared liquid flow among the different geometries (a profile of a channel) under pressure-driven flows. In general, the profile of a microchannel has different geometry such as a rectangle, an isotropically etched shape, and a trapezoid, depending on the fabrication methods. The profile of a microchannel fabricated by excimer laser machining shows a nearly Gaussian shape because of the
distribution of laser beam profile. In this chapter, the liquid flow in a microchannel fabricated by excimer laser machining is estimated. The geometrical effects according to different profiles are examined.

There are two methods to verify liquid flow in a microchannel, microfluidic experimentation and a simulation using CFD (computational fluid dynamics). Deriving an accurate result from a simulation fully relies on physical models and the initial/boundary conditions. In general, CFD uses mass, momentum and energy conservation represented by the Navier-Stokes equations. For a microfluidic simulation, the methods can be used with the proper modification, adding or dropping the terms of dominant forces. The simulation of a microchannel is not a simple problem because a microscale system shows considerably different phenomena compared to a normal scale. As an example, surface tension, capillarity and adhesion force are the dominant forces for the micro/nano scale. These forces can be neglected, on the other hand, in bulk size. In this study, open channels are considered and surface tension is the dominant force for driving liquid. If the part is open, liquid as well as air flows through the channel, called multiphase liquid flow. Multiphase flow means that different, chemically unrelated materials flow through the same channel. These materials might be liquids, gases and tiny solid particles. The primary flowing liquid forms continuous flow. Other flowing materials, on the other hands, may be continuous or just disperse like bubbles or solid particles. For this research, the primary flow is air and the secondary flow is liquid-based material from the inlet. There are several different cases of multiphase liquid flow. When a flowing liquid contains bubbles inside, it is considered to be one case of multiphase
flow [Fuerstman 2007, Hibara 2005]. Another case is the mixture of different liquid flows in the system [Sudarsan 2006]. The liquids filled into the system from different channels can be mixed in the system, flowing together in the same channel. Furthermore, particles flow in primary liquid flow is considered to be multiphase flow. To estimate multiphase flow, experimental and simulated methods can be used. However, the experimental method is very limited due to the size of channel. It is difficult to visualize the liquid flow. Currently, widely used method is to use the velocity in length direction to estimate the liquid velocity. Microfluidic simulation can save time and effort for evaluating the liquid flow. However, the drawback of simulation is the large computation time in extremely large cases. In such cases, only a small part of the entire system is usually simulated. One of the most widely used multiphase (especially, liquid-gas phase) simulation methods is the volume of fluid method (VOF) [Chung 2002]. There are several CFD commercial packages available based on the finite volume method (FVM), including CFD-ACE+, CFX, Flow-3D and Fluent. There is a good study to compare the commercial CFD packages according to several case studies, such as mixing and bubble problems [Glatzel 2008].

In this chapter, the effects of the geometries of microchannels fabricated by laser micromachining will be evaluated using experiment and simulation. The geometries include different depths and widths of microchannels represented as an aspect ratio and a hydraulic radius. After evaluation of the geometrical effect on the liquid behavior, the geometry of microchannels is represented as laser parameters to apply the relationship to
the fabrication of microchannels using laser machining. The results of the study can be used to optimize the design and the fabrication of microfluidic systems, including LOC.

5.2 Geometry of microchannels

The profile of a microchannel can be varied according to the fabrication processes. The different geometries of microchannels can basically be represented by the width and depth. However, a single change in the width or depth may not provide any meaningful effect on many systems. In such cases, an aspect ratio (AR) or a hydraulic radius (HR) may be a good indicator to represent the geometrical changes. Aspect ratio is defined as the ratio between the depth and the width (depth/width). Meanwhile, the hydraulic radius is defined as the ratio between the area of the profile and the length of the profile. Both quantities for a few different geometries are represented in Figure 5.1.

\[
\begin{align*}
AR &= \frac{b}{a} \\
HR &= \frac{ab}{a+2b} \\
HR &= \frac{(a+c)b}{4\sqrt{b^2 + \frac{(a-c)^2}{4} + 2c}} \\
HR &= \frac{ab}{4\sqrt{b^2 + \frac{a^2}{4}}}
\end{align*}
\]

Figure 5.1 The aspect ratio and the hydraulic radius for the different geometries
As mentioned in Chapter 3, the microchannels created by laser micromachining show a nearly Gaussian shape due to the distribution of laser energy profile. Figure 5.2 shows the profile of the microchannel created by laser micromachining.

![Figure 5.2 The profile of microchannel created by laser micromachining](image)

The aspect ratio of the channel profile created by laser micromachining can be defined as $H_{\text{max}}/W$, as shown in Figure 5.2. On the other hand, the hydraulic radius is not as simple to represent as the aspect ratio because the area and length of Gaussian profile must be determined. Hydraulic radius is defined as the ratio between the area of channel cross section and wetted perimeter. Larger hydraulic radius means the wetted perimeter is smaller compared to the cross section area. The Gaussian equation for the profile of a microchannel is expressed as Equation (5.1). $H_{\text{max}}$ indicates the deepest cutting depth in the channel and $\sigma$ is the factor related to the width of channel.

$$f(x) = H_{\text{max}}e^{-\frac{(x-\mu)^2}{(2\sigma^2)}}$$ (5.1)
When $\mu=0$ and $\sigma=W/6$, Equation 5.1 becomes the following

$$f(x) = H_{\text{max}} e^{-18x^2/W^2} \quad (5.2)$$

To find the area of a Gaussian curve, Equation (5.2) is integrated.

$$\text{Area} = \int_{-W/2}^{W/2} H_{\text{max}} e^{-18x^2/W^2} \, dx = \frac{W}{6} H_{\text{max}} \sqrt{2\pi} \quad (5.3)$$

The length of the profile (wetted perimeter-$L$) can be found using the following equations.

$$L = \int_{C} 1 \, ds \quad (5.4)$$

$$L = 2 \int_{0}^{W/2} \sqrt{1 + \left( \frac{-36H_{\text{max}} x e^{-18x^2/W^2}}{W^2} \right)^2} \, dx \quad (5.5)$$

To estimate the length of the profile, the following equation can be used

$$L \approx \Delta x \left[ \sum_{i=1}^{n} \sqrt{1 + \left( \frac{-36H_{\text{max}} x_{i-1} e^{-18x_{i-1}^2/W^2}}{W^2} \right)^2} + \sum_{i=1}^{n} \sqrt{1 + \left( \frac{-36H_{\text{max}} x_{i} e^{-18x_{i}^2/W^2}}{W^2} \right)^2} \right] \quad (5.6)$$

Where, $\Delta x = \frac{W}{2n}$ and $x_i = x_{i-1} + \Delta x$. Equation (5.6) is expressed as follows.
Now, the hydraulic radius for the profile of microchannel created by laser micromachining can be represented as the ratio between Equations (5.3) and (5.7) (Area/L).

\[
L \approx \frac{W}{2n} \left[ 1 + 2 \sum_{i=1}^{n-1} \sqrt{1 - \frac{18H_{\max}(i)e^{-\frac{9}{2n^2i}}}{Wn}} + \sqrt{1 - \frac{18H_{\max}}{W}e^{-\frac{9}{2n}}} \right] \tag{5.7}
\]

5.3 Liquid profile in the microchannel

In Chapter 4, contact angles were measured using mathematical models based on the simplified droplet geometry. In the microchannels, the height and the profile of the liquid surface will be changed by the contact angle. To estimate the liquid behavior such as volume transfer and liquid overflow through the channel, it is important to predict an accurate liquid profile in the microchannel. If the contact angle and the channel geometry are known, the profile of liquid in the channel can be predicted. Figure 5.3 shows the liquid profile in the channel. Initially, the liquid profile is expected to have a certain height with a flat surface (dotted line in Figure 5.3) However, the contact angle prevents liquid from forming a flat surface. The initial height will be changed because of the surface tension force. In other words, the center height of the liquid reduces but the edge height increases as shown in Figure 5.3. It is assumed that the liquid surface is a circular shape and it can be either concave or convex.
To estimate the liquid profile in the channel, simplified geometry for both the channel and the liquid is needed as shown in Figure 5.4. In the figure, $\theta$, $\theta_1$ and $\theta_2$ indicates the
contact angle, the tangent angle of channel and the tangent angle of liquid at the given point respectively. The channel geometry can be expressed via Equation (5.2) and the angle $\theta_1$ can be estimated with Equation (5.8) and (5.9). $W$ and $H_{\text{max}}$ indicate the width and depth of channel, respectively. $x$ indicates the location of the channel in the X direction.

$$f'(x) = \frac{36H_{\text{max}}x}{W^2} e^{-\frac{18x^2}{W^2}}$$  \hspace{1cm} (5.8)

$$\theta_1 = \frac{\pi}{2} - \tan^{-1}\left(\frac{36Hx}{W^2} e^{-\frac{18x^2}{W^2}}\right)$$  \hspace{1cm} (5.9)

If the contact angle $\theta$ is known, $\theta_2$ can be estimated with $\theta_2 = \theta + \theta_1$. The radius of the circular surface of liquid can be calculated with Equation (5.12). If $0 \leq \theta_2 \leq \frac{\pi}{2}$, the liquid surface is concave. When $\frac{\pi}{2} \leq \theta_2 \leq \pi$, it is convex. $k(x)$ indicates the function of the liquid profile in the microchannel.

$$\begin{cases} 
  k(x) = \sqrt{R^2 - x^2} + A & \frac{\pi}{2} \leq \theta_2 \leq \pi \\
  k(x) = -\sqrt{R^2 - x^2} + A & 0 \leq \theta_2 \leq \frac{\pi}{2} 
\end{cases}$$  \hspace{1cm} (5.10)

$$\begin{cases} 
  k'(x) = \frac{-x}{\sqrt{R^2 - x^2}} & \frac{\pi}{2} \leq \theta_2 \leq \pi \\
  k'(x) = \frac{x}{\sqrt{R^2 - x^2}} & 0 \leq \theta_2 \leq \frac{\pi}{2} 
\end{cases}$$  \hspace{1cm} (5.11)

$$\theta_2 = \frac{\pi}{2} - \tan^{-1}\left(\frac{\pm x}{\sqrt{R^2 - x^2}}\right)$$  \hspace{1cm} (5.12)
After $R$ is estimated, $h'$ can be estimated through Equation (5.13).

$$h' = R(1 - \sin \theta_2)$$  \hspace{1cm} (5.13)

Figure 5.5 shows the liquid profile in the microchannel. As the contact angle increases, the liquid profile approaches a flat surface.

![Figure 5.5 Liquid profile in the microchannels according to the contact angle](image)

(a) width=100 and depth=150  \hspace{1cm} (b) width=150 and depth=100

Figure 5.5 Liquid profile in the microchannels according to the contact angle

### 5.4 Liquid flow in different geometries of microchannel

#### 5.4.1 Fabrication of microchannels and experiment of liquid behavior

To observe the liquid flow through microchannels with different geometries (different aspect ratios and hydraulic radii), several microchannels were fabricated on
polyethylene as shown in Figures 5.6 and 5.7. To create different geometries, a different aperture size and different number of laser pulses per area were used based on the parametric study in Chapter 3. Table 5.1 indicates widths and depths of the microchannels, and the aspect ratios and hydraulic radii were also estimated using Equations (5.3) and (5.7) to represent the different geometries. To visualize the liquid flow in the channel, ethanol mixed with fluorescent dye flowed through the channels. The reservoir is filled with liquid and recorded the liquid flow through the microchannels using a CCD as shown in Chapter 3. The velocity of each liquid in the length direction was calculated to determine the liquid behavior in the channels. The positions of liquid flow were measured at 0.1s time intervals and the velocity was estimated.

Figure 5.6 Microchannels fabricated by laser micromachining
Figure 5.7 Geometries of microchannels according to different widths and depths (using different machining parameters)

Table 5.1 Geometries of microchannels, aspect ratio and hydraulic radius (unit: µm)

<table>
<thead>
<tr>
<th></th>
<th>Width</th>
<th>Depth</th>
<th>Aspect ratio</th>
<th>Hydraulic radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel 1</td>
<td>64</td>
<td>48</td>
<td>0.75</td>
<td>10.7</td>
</tr>
<tr>
<td>Channel 2</td>
<td>96</td>
<td>99</td>
<td>1.03</td>
<td>17.4</td>
</tr>
<tr>
<td>Channel 3</td>
<td>100</td>
<td>62</td>
<td>0.62</td>
<td>15.5</td>
</tr>
<tr>
<td>Channel 4</td>
<td>122</td>
<td>114</td>
<td>0.93</td>
<td>21.7</td>
</tr>
<tr>
<td>Channel 5</td>
<td>141</td>
<td>159</td>
<td>1.13</td>
<td>26.1</td>
</tr>
</tbody>
</table>

5.4.2 Results of microfluidic experiments

Figures 5.8 and 5.9 represent the velocity and travel distance of liquid flow. The liquid velocity was measured during the first 1s. The velocity in all cases gradually decreased as the liquid travelled through the microchannels. There are possible two
factors to estimate the geometry of a microchannel: aspect ratio and a hydraulic radius, as mentioned in Table 5.1. The liquid velocity was estimated according to these two factors as shown in Figure 5.10. The experiment was conducted five times for each case. The differences between each trial can be explained with measurement error and slightly different experiment conditions. The results revealed that the liquid flow is more developed in the channel with a higher hydraulic radius; however, a higher aspect ratio does not guarantee a higher mean velocity. Thus, if the area of the profile of two microchannels is the same, the microchannel with a higher hydraulic radius can provide a higher flow rate.

Figure 5.8 Liquid velocity in microchannels
Figure 5.9 Travel distance for liquid in each microchannel according to time and mean velocity
Figure 5.10 Mean velocity of liquid flow according to the geometry of channels

(a) Mean velocity of liquid flow according to the aspect ratio of channel

(b) Mean velocity of liquid flow according to the hydraulic radius of channel
Figure 5.11 shows the travel time according to the hydraulic radius to the particular point of microchannel from the inlet of microchannel. The figure shows the arrival time for liquid at two different locations. A higher hydraulic radius yields shorter arrival time at the both location. The results fairly matched the following equation deriving from Equation (3.10). $y, R_h, \gamma, \mu$ and $\theta$ indicate a travel distance, a hydraulic radius, surface tension coefficient, viscosity and a contact angle.

\[
\int_0^y y\,dy = \int_0^t \frac{R_h \gamma \cos \theta}{4\mu} \,dt \\
(5.14)
\]

\[
t = \frac{2\mu y^2}{R_h \gamma \cos \theta} \\
(5.15)
\]
5.4.3 Simulation study of liquid flow in microchannels

Volume of fluid (VOF) is a very powerful method for a multiphase model such as a free surface model [Liovic 2001, Hirt 1981]. Several commercial CFD packages generally support multiphase simulation. The simulation begins from the continuity and momentum equations as represented in Equations (5.16) and (5.17). In this research, the surface tension force is the only driven force for the model because all other forces are not appropriate to apply to the system. Therefore, the force generated by the surface tension is included in Equation (5.17). Furthermore, the body force, shear stress and pressure terms exist in Equation (5.17).

\[
\frac{\partial \rho}{\partial t} + \nabla (\rho u) = 0 \tag{5.16}
\]

\(\rho\) and \(u\) indicate the density and velocity of the mixture material for a multiphase model.

\[
\rho \left[ \frac{\partial u}{\partial t} + u \cdot \nabla u \right] = -\nabla p + \mu \nabla^2 u + f_b + f_s \tag{5.17}
\]

\(p, \mu, f_b\) and \(f_s\) represent pressure, viscosity of the mixture of air and primary liquid, a body force and a force from the surface tension in a multiphase model. The body force is represented by gravity acceleration as \(\rho g\). Figure 5.12 describes the geometry of microchannels after mesh generation for the simulation. Ethanol flows from the inlet to
the outlet, driven by the surface tension force. The top surface of the channel is exposed to the environmental conditions. Thus, the flow in the channel can be considered to be a multiphase liquid flow. The volume fraction of ethanol in the inlet and the static contact angle on the wetting wall are given as initial boundary conditions for the simulation. Due to limited computational time, liquid behavior was estimated for only the first 2mm length of each channel. It is assumed that the flow in the channel is laminar because Reynolds number is extremely low.

![Mesh generation on the microchannel](image)

**Figure 5.12 Mesh generation on the microchannel**

### 5.4.4 Results of simulation

Figure 5.13 indicates the volume of ethanol in the microchannel during the liquid flow. To represent the volume of ethanol, channel 5 in Table 5.1 was used. The volume of ethanol was estimated on the center plane of the microchannel. The blue color in Figure 5.13 indicates air from the open top part. The top part of channel is dominated by air. On the other hand, the ethanol volume increases as the depth approaches the bottom. Five different X locations (0, 0.4, 0.8, 1.2 and 1.6mm) were checked. The volume of ethanol decreases as liquid flow approaches the outlet.
(a) Volume of ethanol in the microchannel: rectangular display on the center plane in flow direction and Gaussian display on the outlet.

(b) The volume fraction of ethanol at the different X locations

Figure 5.13 Volume fraction of ethanol in the microchannel during the liquid flow

Figure 5.14 represents the liquid velocity. The center line of the microchannel was used to represent liquid velocity (using the center line below 0.035mm from the free surface of ethanol because it is shown that ethanol fills the entire volume in most cases). The
velocity gradually decreases as liquid flow develops in the X direction. Each channel has a different inlet velocity because different surface tension is applied according to the geometry. It is revealed that higher surface tension develops on the higher hydraulic radius. Once velocity develops, shear stress is generated against the liquid flow due to the viscosity of liquid, so the velocity gradually decreases.

Figure 5.14 Liquid velocity of ethanol through the different channels

The results of velocity in simulation show the same trend as with the experimental results. The different magnitude of velocity between experiments and simulation may be explained by the limited experimental measurement. It is obvious that the different mean velocity of each channel is due to different velocity at the beginning of liquid development
5.5 Relationship between the laser machining parameters and the channel geometry

So far, It is estimated that the laser parameters would create an exact geometry based on the design. Furthermore, the geometrical effects of microchannels were examined to apply the results to the design of microchannels for bio-medical devices. Figure 5.17 represents the relationship between the hydraulic radius and number of laser pulses based on the laser parametric study when the width of the microchannel is fixed. In general, microsystems are created in a limited area, so the width is more critical than the depth. Figure 5.17 indicates that the hydraulic increases as the number of laser pulses increases. However, if the number of laser pulses is over a certain amount, the hydraulic radius is not greatly changed.

![Figure 5.15 Hydraulic radius vs Number of laser pulses](image)

Figure 5.15 Hydraulic radius vs Number of laser pulses
The relationship between hydraulic radius and the number of laser pulses can be represented by the following equations. Hydraulic radius is proportional to the logarithm value of the number of laser pulses.

\[ R_h = a \ln(n) + b \]  \hspace{1cm} (5.18)

\[ n = e^{\frac{R_h - b}{a}} \]  \hspace{1cm} (5.19)

a and b are constant values dependent on the type of laser and the materials used for machining. n indicates the number of laser pulses. The number of laser pulses can be represented by hydraulic radius and a few constants. By substituting Equation (5.18) into Equation (3.10), the liquid velocity can be expressed in terms of laser machining parameters (numbers of laser pulse) as in Equation (5.19).

\[ V = \frac{dy}{dt} = \frac{(a \ln(n) + b) \gamma \cos\theta}{4\mu y} \]  \hspace{1cm} (5.20)

The equation can be used to predict liquid velocity according to the laser parameters instead of according to the hydraulic radius. Figure 5.18 represents the liquid velocity according to number of laser pulses at given travel distances.
5.6 Summary

In this chapter, experiments and a simulation of microchannels have been conducted to evaluate the design of microchannels. It is revealed that different geometry of microchannels shows the different velocity of liquid flow. To check the experimental results, simulation was performed and the results show that the liquid velocity in the X direction gradually decreases, similar to the experimental result. The results agree with experiment in that a higher hydraulic radius provides a higher mean velocity during the liquid flow due to the effect of higher surface tension. Thus, for more effective liquid delivery, a higher hydraulic radius is essential. In this study, after the design of the microchannel was evaluated by liquid flow, the relationship between the channel geometry in terms of hydraulic radius and the laser parameter was derived. The result can be used for optimization of the design and fabrication of microsystems.
CHAPTER 6: MICROFLUIDIC APPLICATION

INKWELL FABRICATED BY LASER MICROMACHINING FOR DIP-PEN NANOLITHOGRAPHY AND GENERATION OF NANOSTRUCTURE

In this chapter, the application of microchannel systems created by excimer laser micromachining is presented. This work concentrates on the fabrication of the inkwell for dip-pen nanolithography (DPN) using laser micromachining to simplify current fabrication methods of Inkwell. Laser micromachining can overcome a few drawbacks of current fabrication methods. For the proposed inkwell, it is created on silicon substrate (100) by laser micromachining. To verify the inkwell, DPN is performed to generate 16-mercaptohexadecanoic acid (MHA) patterns on a silicon substrate coated with a thin gold layer using an AFM tip coated with inkwell. MHA patterns were used to create nanostructures (gold dot arrays) by wet chemical etching and reactive ion etching (RIE).

6.1 Introduction

Dip-pen nanolithography (DPN) is a nanofabrication method for creating tiny size patterns using atomic force microscopy (AFM). It can create nanopatterns or
nanostructures with various materials ranging from nanoparticles to polymers. A coated AFM tip is used to transfer a certain material to a substrate using physical contact between the tip and the substrate along the tip movement to generate nanopatterns or nanostructures. Inking indicates that the AFM tip is to be coated with a certain material. It is the first step in the DPN process. To maintain the constant supplement and a constant diffusion rate of the coated material to the substrate during DPN, a proper inking method must be applied. Currently, the most prevalent method is liquid phase dip inking because it is simple and easy to implement. In this method, AFM tip needs to be dipped into the material source and the overcoated material is blown out using nitrogen gas. However, it causes a non-uniform and an uncontrollable inking and result in a non-uniform writing rate during the process [Li 2006]. It may also break the tip due to hold too much volume. Furthermore, it must be taken out from the main body of AFM whenever it needs to be recoated with materials. To solve these problems, several researchers have proposed new inking methods such as vapor inking and inking using microchannels and a reservoir [Li 2006, Moldovan 2006b, Rivas-Cardona 2007].

Li et al. (2006) proposed the vapor inking method. This system consists of a container, fluidic networks and a reservoir. To coat a tip using this method, the tip approaches the reservoir and is then located on the top of the reservoir. Once the tip reaches the reservoir, the bottom of the reservoir is heated to generate vapor of the material and this vapor then moves from the reservoir to the tip. This solves a few current problems of the dip inking method. However, the inking system involves complicated serial fabrication processes and it is also hard to achieve the necessary physical alignment
between the reservoir and the AFM tip during the process. In addition, the materials are able to be coated with this method are limited because of the heating step. For example, biomaterials such as protein can be destroyed during heating. The second method is to create an ink reservoir directly connected to an AFM tip for a uniform and controlled supplement of materials. This is termed of “nanofountain pen” [Moldovan 2006b]. This method has been developed for a single tip as well as multiple tips. Currently, it has been extended up to 12 tip array pens [Moldovan 2006a]. This method can transfer materials onto a substrate directly from the material source through the channel that connects the AFM tip and the reservoir. Several materials have been deposited using the coating method. For example, MHA (16-mercaptohexadecanoic acid) patterns on gold substrates are generated with a nanofountain pen and it has also been reported that gold nanoparticles on oxidized silicon substrates can be deposited [Wu 2007]. Although it has several advantages over other methods, the fabrication processes are highly complicated, which include several different wet or dry etchings, and liquid flow through a tiny channel to deliver materials is a critical issue. The third method is to use a multiple microwell array to coat the AFM tip. Tiny microwells are fabricated and microbeads of polyethylene glycol (PEG) are placed into the wells to prevent the evaporation of materials [Rivas-Cardona 2007]. Commercial Peltier coolers (thermoelectric modules) are located under a microwell substrate to maintain a low temperature. The Peltier coolers reduce the temperature in the microwell below the dew point, and water droplets generated on microbeads of polyethylene glycol (PEG) prevent the evaporation of materials from the microwells. However, manipulating a micro-sized PEG to place into a
microwell is painful. In addition, the microwell cannot preserve a large volume of material for DPN. Another dip inking method has been developed by NanoInk Inc. [Rosner 2006]. They fabricated a small inkwell consisting of microwells, channels and reservoirs. Dip inking takes place at the microwell, and the channel delivers ink from the reservoir to the microwell. The microwell has an individual channel and reservoir, so it can be used to coat multiple inks (different materials) simultaneously. The inkwell system is fabricated by deep reactive ion etching to achieve a high aspect ratio.

The above four methods can provide several advantages. However, fabrication processes are generally highly complicated and hard to implement. The dip inking method is still frequently used for DPN because of these reasons. In this research, dip inking method using inkwells were proposed and the inkwell is fabricated by excimer laser machining, which can make the fabrication process significantly simpler and easier. To verify the inkwells, AFM tip is coated with MHA. After that, MHA patterns were generated on a gold-coated silicon substrate using DPN. The MHA patterns on the gold substrate are used as masks for wet etching and dry etching to create nanostructures.

### 6.2 Design and fabrication of inkwell

Inkwell consists of three components - a reservoir, a microchannel and a small pocket as shown in Figure 6.1 (a). The reservoir and the pocket are connected to the channel to deliver material from the reservoir to the pocket. Once the material is filled into the reservoir using a micropipette, it can flow from the reservoir to the pocket through the channel. After the material reaches the pocket, the AFM tip approaches the
pocket to be coated as shown in Figure 6.1 (b). The diameter of the reservoir is 2 mm, channel length is 4 mm, the channel width is 120 µm, the depth of the system is 100 µm and the size of the pocket is 270×380 µm². This design is easily extended for multiple AFM tips by changing the shape of components and adding more components to the system.

Based on the inkwell design, it was generated by excimer laser micromachining (ArF-193 nm UV laser pulse). Laser micromachining can directly create any complex microstructure, even structures with different depths. By contrast, creating microstructures with different depths using traditional microfabrication methods such as wet/dry etchings can be a problem. Furthermore, laser micromachining is easy to implement and produces no toxic residual products. A lab-built micromachining system consisting of a commercial laser scribe (COMPexPro 201, Coherent Inc.) and a three-
axis micropositioning stage (A320, Aerotech Inc.) was used to create the inkwell. The system is operated with the traditional G-code for tool paths. The desired structures can be easily generated along the tool path of the laser spot. The inkwell was created on silicon substrate (100), which is frequently used for micro- and nanofabrication processes. Before laser micromachining, the silicon substrate was cleaned properly using acetone and methanol in an ultrasonic bath each for 3 min. Figure 6.2 shows images of the inkwell after fabrication by laser micromachining.

![Figure 6.2 Inkwell fabricated by laser micromachining](image)

**6.3 Liquid flow through the microchannel**

Inkwell must allow well-developed liquid flow through a microchannel. This is the most important issue for systems using microchannels. In general, there are two issues in using laser micromachining over traditional microfabrication processes- high surface roughness and a different microchannel profile (Gaussian shape). To verify liquid
flow in the system, liquid flow was checked using fluorescent dye and a UV black light. MHA was mixed with a tiny volume of fluorescent dye and filled into the reservoir. It was observed that the MHA flowed through the channel without any unexpected result. However, the overflow was observed around the reservoir. Figure 6.3 shows the image of the MHA flow into the inkwell. Figure 6.3 (a) shows the liquid front (obtained by optical microscope) and 6.3 (b) represents the liquid flow using fluorescent dye (violet color) after liquid flow is completed.

Figure 6.3 Images of MHA flow into the inkwell

6.4 Using inkwell for DPN

6.4.1 Setup for the inkwell process

To validate the inkwell fabricated by laser micromachining, MHA patterns were generated on a gold substrate and then nanostructures were generated by wet etching. MHA and a gold substrate were selected for experiment because they are the most
prevalent and popular combination for DPN and several different applications, such as organic masking for chemical etching and protein patterning, have been reported [Zhang 2007]. MHA and the gold-coated silicon substrate were purchased from Sigma-Aldrich. The NSCRIPTOR DPN system (NanoInk Inc.) shown in Figure 6.4 was used for this research.

![Image](nscriptor.png)

(a) NSCRIPTOR DPN system (NanoInk Inc.) (b) Inkwell setup on the AFM stage

Figure 6.4 Inkwell setup and the silicon substrate on the AFM stage

As the first step, MHA was filled into the reservoir using a micropipette. The inkwell and gold substrate were then placed on the AFM stage together. The substrate was cleaned with DI water and nitrogen gas to remove contamination before being placed on the AFM stage. Once the AFM tip approached the substrate, the inking process can be performed as shown in Figure 6.5. During the inking process, the pocket can be easily found by the optical microscope built in the AFM system. Figure 6.6 demonstrates the alignment between the tip and inkwell as the AFM tip approaches the pocket. After the inking process was completed, the tip returned to the substrate. Right after the AFM tip
was coated, MHA dot patterns were generated. To create the patterns, the AFM tip stayed on each point for 20 s (dwell time). Temperature was 23.5°C and humidity was 40.3%.

Figure 6.5 Description of the DPN inking process

Figure 6.6 Alignment between the AFM tip and inkwell
6.4.2 MHA pattern generation

Figure 6.7 (a) shows the image of a single MHA dot and Figure 6.7 (b) shows several dots at different locations. Each dot has 5 µm diameter and the scan range of Figure 6.7 (b) is 50×50 µm². The experimental result indicated that the AFM tip was properly coated by the fabricated inkwell.

![MHA patterns](image)

(a) MHA single dot    (b) MHA dots at different locations    (c) Topological images of (b)

Figure 6.7 MHA patterns generated on a gold substrate

6.4.3 Nanostructure generation on the silicon substrate using wet chemical etching

One of the earliest applications of DPN was to generate masking for wet chemical etching [Weinberger 2000]. MHA patterns on the gold substrate can be used as masks on a silicon substrate for wet chemical etching. The MHA layer can protect a gold layer against wet chemical etching. After wet etching, the MHA patterning area remains on the gold substrate. The substrate has three layers- gold, titanium and silicon. Thus, two
different etching processes are necessary for the gold and titanium layers. The titanium layer is generally used to provide an adhesion effect between the gold and silicon. To remove the gold layer, the following recipe for an iron nitrate/thiourea etchant is used to etch a gold film [Wei 2007]:

\[
\begin{align*}
A &= 2.66 \text{ mM Fe(NO}_3)_3 \text{ in octanol-saturated H}_2\text{O} \\
B &= 40.0 \text{ mM Thiourea in octanol-saturated H}_2\text{O} \\
\text{Recipe ratio: } 2.5 \text{ mL A + 2.5 mL B + 15 }\mu\text{L HCL} \\
\text{Etching rate: 4–6 nm/min}
\end{align*}
\]

To etch out the titanium adhesion layer, aqueous HF was used in the following recipe:

\[
\begin{align*}
0.5\% \text{ HF (diluted in deionized water)} \\
\text{Recipe ratio: } 5.0 \text{ mL H}_2\text{O + 0.1 mL HF (49\%)} \\
\text{Etching rate: 6 nm/min}
\end{align*}
\]

Before wet chemical etching, the substrate was blown out with nitrogen gas to remove any contamination. Based on the etching rate of iron nitrate/thiourea, it took approximately 25 min to remove 100 nm of the gold layer, but only a few minutes to etch the titanium adhesion layer. Figures 6.8 and 6.9 show images of the gold structures generated on a silicon substrate by wet chemical etching.
15 s dwell time    10 s dwell time    5 s dwell time    3 s dwell time

1 s dwell time    0.5 s dwell time

Figure 6.8 AFM images of gold dots on the silicon substrates
Figure 6.9 Topological images of the gold dot patterns on the silicon substrates
6.4.4 Nanostructure generation using reactive ion etching

So far, gold patterns have been generated with DPN and wet etching. The gold patterns have important roles as mask resists for reactive ion etching (RIE). Dry etching such as RIE can transfer patterns to the substrates. There are two important issues of RIE for a silicon substrate. The first one is to select a recipe of RIE. Currently, there are several recipes available [Köhler 1999]. It mainly uses SF$_6$, CF$_4$ or Cl$_2$ with 10-100mtorr pressure for a silicon etching. The other issue is to select a proper material for a mask generation because of the poor selectivity of RIE. In general, almost infinite selectivity is possible in using metal masks (except e.g. Ti, Mo, W, Nb, and Ta for F-based plasmas and Al or Cr for Cl-based plasmas), photoresist and silicon oxide [Jansen 1996, Wang 2002]. Gold mask patterns have been reported for RIE [Ovchinnikov 1999, Zhang 2006]. SF$_6$ is mainly used to etch a silicon substrate for this study. The etching rate increases as power and gas flow increase [de Boer 2002]. However, SF$_6$ tends to be less anisotropic etching in ambient temperature. For experiments, semigroup 1000TP which is a parallel plate reactive ion etch system was used to etch silicon substrates. There are three available gases in the system, which are SF$_8$, CHF$_4$, O$_2$ and Ar. SF6 (4 sccm), 100W (power) and 80mtorr (pressure) were used for the process. RIE gives more anisotropic etching compared to wet chemical etching. RIE can provide poor selectivity during processes. It means that a gold layer will be etched out during the processes. However, the gold layer might be sufficiently strong and thick enough to withstand RIE during the processes. The duration of the etching process can be controlled to increase or decrease the etching depth of the silicon substrate. Figure 6.10 represents the dot pattern before
and after RIE. The pattern was created with 10s dwell time for each single dot. The depth of etching is approximated between 40 and 50nm. RIE was operated for 24s.

(a) Gold dot pattern on a silicon substrate before RIE

(b) Gold dot pattern on a silicon substrate after RIE

Figure 6.10 AFM images of a gold dot array on a silicon substrate before and after RIE
6.5 Summary

In this chapter, inkwell was successfully created on a silicon substrate for DPN using laser micromachining. Several current methods for fabricating an inking system involve complex microfabrication processes such as serial etching methods. By contrast, laser micromachining is relatively simple and easy to implement and can successfully replace current fabrication processes to create inkwell. After generating inkwell, MHA patterns were created on a gold-coated silicon substrate to verify the method. Furthermore, the MHA patterns were used to create gold structures on silicon substrates using wet/dry etching. The final structures could be used to create other applications, including magnetic nanostructures combined with other methods such as pulsed laser deposition (PLD). This research revealed that laser micromachining could be used to fabricate inkwells with less effort compared with other fabrication methods. It can also create inkwells for multiple-pen arrays with a simple design change. However, a few drawbacks were recognized during the research. Evaporation must be prevented by properly covering the reservoir, and the overflow around the system must be considered by using structures with a high depth.
CHAPTER 7
CONCLUSION AND FUTURE RESEARCH

In this research, primary focus was the excimer laser micromachining, including machining parameters studies and microfluidic applications created by laser micromachining. The primary objective of the research is to apply excimer laser micromachining to fabricate microfluidic devices. Laser micromachining parameters were estimated on a few different materials to apply to fabricate microfluidic systems. The laser micromachining was used to create a simply microfluidic systems and the liquid flow was observed in the system by using both experiment and simulation. Furthermore, the channel geometry related to liquid flow was linked with laser machining parameters. In the last part of paper, microfluidic systems created by laser machining were applied to dip-pen nanolithography for the coating process. In the chapter, the results were summarized and future research direction is discussed.

7.1 Conclusions

The laser micromachining and microfluidic study were performed in previous several chapters, including laser micromachining and functionality of system. The research was divided in several sub-topics. Following is the summary of the results of this research work.

1) *Parametric study of laser micromachining:* Before fabricating by Excimer laser
machining, the machining parameter related to the material removal rate must be examined. It was estimated three different materials with a few different machining parameters, including laser intensity, aperture size and number of laser pulses per area. It is obvious that a higher energy level and a larger aperture size provide a higher material removal rate in depth direction. In addition, the material removal rate is proportional to number of laser pulses.

2) **Microfluidic experiments on microchannels created by laser micromachining:**

After study for machining parameters, the simple reservoir and microchannels were fabricated on different materials. After the systems were fabricated microfluidic experiments were performed using three different liquids (water, ethanol and glycerine) on the created microchannels. Only surface tension force is the dominant factor to develop liquid flow in the research. Even if the materials have different properties such as surface tension, density and viscosity, liquid flow is well developed but shows the different velocity in the length direction.

3) **Geometrical method to measure contact angles:** A new method is developed to estimate a contact angle on the solid surface. Math models were derived based on the simplified geometry of a liquid droplet. When a droplet volume is large, the gravity effect is not negligible so two math models were derived with and without gravity effect. The contact angle without the gravity effect is merely dependent on the wetting distance and the droplet volume. On the other hand, the material properties included density and surface must be considered when gravity effect is not negligible. The proposed models were checked by current methods for
measuring contact angles. It is revealed that the method is correct compared to the current method within 13% error. The measure contact angle can be used to predict the liquid behavior and the liquid profile in the microchannel. Furthermore, the method can be used to design and evaluate microarray and microfluidic systems.

4) **Estimated the effect of geometries of microchannels using experimental and simulated methods and the relationship between the channel geometry and laser machining parameters:** The geometry of microchannel influences the liquid behavior. The geometry of channel can be expressed as an aspect ratio and a hydraulic radius. To check the effect of geometry to the liquid flow, five different channels were fabricated by excimer laser micromachining. Following experiments and simulation studies were conducted. The results show that a higher hydraulic radius supports a higher liquid velocity. **The revealed geometrical effect on microchannel (functionality of liquid flow) was linked to laser machining parameters and it can be used in the fabrication and the design stage for systems for using laser micromachining.**

5) **Develop microfluidic application – Inkwell for DPN (Dip-Pen Nanolithography):**

To develop the coating method for DPN, excimer laser micromachining was used to create microfluidic systems on a silicon substrate. The coating process was conducted to verify the proposed method. Furthermore, patterns in nano size were created combined with DPN and wet/dry etching. **It is revealed that this method properly coats the AFM tip for DPN, and provides several advantages such as easy implementation and simple fabrication.**
7.2 Future research work

So far, the results of this research work were summarized. It mainly focuses on excimer laser micromachining and microfluidic applications. In this research, the possibility has opened the door to use excimer laser technology for microfluidic applications. Behind this research, there are several possibilities for future research works. Following is the list of future research.

1) Improvement of machining quality for semiconductors and metals:
Nano-second laser was used for this study. However, it is difficult to produce the high quality machining surface on semiconductor and metals because the heat effect is dominant on the materials. A candidate is to reduce the duration of laser pulse like femto-second laser. It can decrease the heat effect compared to other laser technology such as nano-second laser.

2) Laser parametric study with thermal effect: Thermal effect on laser machining is critical issues especially for metals and semiconductors. However, currently most studies do not handle the problem because of high complexity. However, more accurate result of parametric study, it must be addressed.

3) Developed an automated laser system for 3D structures fabrication: The laser micromachining parameters should be reflected in real time to create 3D structures. For example, the energy level or repetition should increase to create the higher depth, and the aperture size should be changed to generate the different width. The fully automated laser system makes it easy to
fabricate a higher complex structure.

4) **Microfluidic experiment and simulation with biomaterials**: The liquid behavior was estimated on the microchannel using ethanol and water instead of biomaterials. In this study, biocompatible materials such as polyethylene were used to create microchannels. Thus, the biomaterials such as protein and blood can be tested on microchannels because the final objective of this study is to use excimer laser technology for bio-devices such as Lab-on-a-chip (LOC).

5) **Developed design of microfluidic systems for biomedical applications**: In this study, a simple microfluidic system consisted of a reservoir and a microchannel was tested. However, the complex design must be developed for the real application. As an example, two different materials should be put into the system and mixed in the system for some applications. In the case, the length of channel should be changed for enough mixing. For LOC, the material from inlet should be reached either a microarray or nanoarray in the target area. The design should carefully be developed to deliver materials to each single array.

6) **Development of inkwell to prevent evaporation**: The inkwell was created to coat AFM tip for DPN. It was proved that the proposed method can coat materials on the tip successfully. However, the evaporation from the system cannot be prevented with current methods. It is essential to prevent evaporation for more reliable system.
REFERENCES


