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Femtosecond laser processing of photovoltaic and transparent materials

By

Sanghoon Ahn

A dissertation submitted in partial satisfaction of the
requirements for the degree of
Doctor of Philosophy
in
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in the
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of the
University of California, Berkeley

Committee in charge:

Professor Costas P. Grigoropoulos, Chair
Professor Ralph Greif
Professor Andrew Minor

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Femtosecond laser processing of photovoltaic and transparent materials

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By

Sanghoon Ahn
Abstract

Femtosecond laser processing of photovoltaic and transparent materials
by
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The photovoltaic semiconducting and transparent dielectric materials are of high interest in current industry. Femtosecond laser processing can be an effective technique to fabricate such materials since non-linear photochemical mechanisms predominantly occur. In this series of studies, femtosecond (fs) laser processing techniques that include laser drilling on Si wafer, laser scribing on CIGS thin film, laser ablation on Lithium Niobate (LN) crystal, and fabrication of 3D structures in fused silica were studied.

The fs laser drilling on Si wafer was performed to fabricate via holes for wrap-through PV devices. For reduction of the number of shots in fs laser drilling process, self-action of laser light in the air was initiated. To understand physical phenomena during laser drilling, scanning electron microscopy (SEM), emission, and shadowgraph images were studied. The result indicated the presence of two mechanisms that include fabrication by self-guided beam and wall-guided beam. Based on our study, we could fabricate ~16 µm circular-shaped via holes with ~200 laser pulses on 160-170 µm thick c- and mc-Si wafer.

For the fs laser scribing on ink jet printed CIGS thin film solar cell, the effect of various parameters that include pulse accumulation, wavelength, pulse energy, and overlapping were elucidated. In our processing regime, the effect of wavelength could be diminished due to compensation between beam size, pulse accumulation, energy fluence, and the absorption coefficient. On the other hand, for high PRF fs laser processing, pulse accumulation effect cannot be ignored, while it can be negligible in low PRF fs laser processing. The result indicated the presence of a critical energy fluence for initiating delamination of CIGS layer. To avoid delamination and fabricate fine isolation lines, the overlapping method can be applied. With this method, ~1 µm width isolation lines were fabricated.

The fs laser ablation on LN wafer was studied. The ablation thresholds and laser induced periodic surface structure (LIPSS) patterns according to the angle between laser polarization and crystal orientation were elucidated via SEM images. We could observe that both the ablation threshold and the LIPSS patterns were affected by the angle between laser polarization and crystal orientation. Additionally, we could fabricate ~45 nm dots on z-cut LN wafer surface along the x-axis.

Finally, 3D helical microchannel was fabricated in fused silica and utilized for protein mixing. The channel of ~50 µm diameter was fabricated by the femtosecond laser irradiation and chemical etching (FLICE) technique. For understanding of fluidic motions, numerical analysis was performed. The numerical analysis indicates the existence of an effective mixing condition due to compensation between residence time of the flow in the channel and the transverse flow patterns. Experiments supported the
numerical analysis and we could achieve 90% mixing within ~400 µm distance from the confluence of two streams.
To Yeonkyung, Jayden Junu, parents and God
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Table 2-1. Classification of absorption mechanism in this dissertation. (SPA: single-photon absorption, TPA: two-photon absorption, and MPA: multi-photon absorption)
List of symbols

- $\alpha_{av}$: Constant (avalanche ionization)
- $\beta_{av}$: The avalanche ionization rate
- $\gamma$: Liu-Masilyah number
- $\gamma^\ast$: Modified Liu-Masilyah number
- $\gamma_{Ke}$: Keldysh parameter
- $\delta$: Normalized curvature ($kr$)
- $\varepsilon_0$: Vacuum permittivity
- $\eta$: Normalized torsion ($\tau hr$)
- $\eta_{water}$: The water viscosity
- $\kappa$: The helix curvature
- $\Lambda$: Period of laser induced periodic structures on surface (LIPSS)
- $\lambda$: Wavelength of laser pulse
- $\lambda_0$: Wavelength of light in vacuum
- $\lambda_{em}$: Emission wavelength
- $\lambda_{ex}$: Excitation wavelength
- $\sigma^{(m)}$: The cross section of $m$-photon absorption for excitation of a valence-band electron to conduction band
- $\tau$: Laser pulse duration
- $\tau_h$: The helix torsion
- $\omega$: Angular frequency of laser light
- $\omega_0$: Gaussian beam waist
- $\hbar$: Plank constant
- $\hbar\omega$: Photon energy
- $C_S$: Concentration of Streptavidin-Alexa conjugates (mol/m$^3$)
- $C_R$: Concentration of Rhodamine B (mol/m$^3$)
- $D$: Diameter
- $D_{diff}$: The diffusion coefficient of the fluorescing agent
- $D_R$: The diffusion coefficient of Rhodamine B
- $D_S$: The diffusion coefficient of Streptavidin-Alexa conjugates
- $d$: Diameter of the circular channel
- $E$: Pulse energy
- $E_k$: Kinetic energy of excited electrons in conduction band
- $E_g$: Bandgap of material
- $E_{max}$: Maximum pulse energy
- $F$: Pulse energy fluence
- $F_{th}$: Ablation threshold
- $I$: The laser intensity
- $I_i$: The normalized intensity at $i^{th}$ pixel with respect to maximum intensity
- $I_{perf.mix}^i$: Intensity values for the perfect mixing
- $I_i^0$: Intensity values for the zero diffusion
- $2\pi K$: The helix pitch
- $k$: The Boltzmann constant
- $l$: The effective penetration depth
The smallest number of photon to satisfy the relation \( m(\hbar \omega) > E_g \)

**Effective mass of electron**

**Electron density**

**The characteristic plasma density**

**The total number of pixels**

**Refractive index of material**

**Linear (or low-intensity) refractive index**

**Nonlinear refractive index**

**Critical power for generation of self-trapping**

**The rate of multiphoton absorption**

**The flow rate**

**The helix radius**

**Radius of Streptavidin**

**The radius of the circular cross section**

**The diffusion time**

**The mean flow velocity**

**The mean velocity of flow in channel**

**The entry length**

**Ablation depth**

**The characteristic length**

**Dean number**

**Germano number**

**Reynolds number**

**The Schmidt number**
Chapter 1

Introduction

Laser has attracted interest as a material processing tool for modern industry due to its unique properties such as monochromaticity, spatial/temporal coherence, and collimation. The monochromaticity combined with choice of wavelength can enhance the processing efficiency and the possibility of selective material processing. The spatial coherence can enhance the high energy density (J/cm²) of processing beam via focusing of laser light, and the collimation can initiate the noncontact material processing. With these unique properties, laser opens up possibilities of new processing techniques that are difficult to achieve by conventional material processing methods. [1, 2] The new processing techniques include laser drilling on thin and brittle material, laser scribing on thin film with low adhesion layers, fabrication of nano-scale surface structure, fabrication of three dimensional (3D) structure inside a semi-transparent material, etc. In this series of studies, laser-processing techniques are applied to photovoltaic (PV) semiconducting materials (crystalline and multicrystalline silicon, and copper-indium-gallium-selenide) and dielectric transparent materials (lithium niobate and fused silica).

PV devices have been investigated as a renewable energy source due to depletion of fossil fuels and various environmental issues. One of the most important parameter of PV device is the efficiency. In order to approach the theoretical efficiencies of PV materials, several attempts can be performed such as increasing the amount of light collected by the cell, increasing the collection of light-generated carriers, minimizing the forward bias dark current, and minimizing resistive losses on the current path.[3] Among these attempts, increasing the light coupling is related with fabrication of PV devices. The conventional PV devices have front electrode for collecting light-generated carriers and initiating electric current. However, these electrodes generate shadows underneath (so called dead zone) and reduce the total amount of sunlight, hence causing reduction of efficiency. Therefore, to increase the efficiency, the dead zone should be minimized. To minimize the dead zone, warp-through PV devices were proposed.[4, 5] For warp-through PV device, silicon (Si) is chosen as active material since it is the second most abundant material in the earth and it has relatively high theoretical efficiency limit (~29%).[6] The wrap-through PV requires 10,000-25,000 via holes in one panel (154×154 mm) as electrode.[5] Meanwhile, Si based PV devices have thin active layers (~100 – 200 µm) due to compensation between diffusion length of light-generated carriers and absorption depth of sunlight.[7-9] Therefore, via holes should be fabricated on thin and brittle wafer. This cannot be achieved by conventional drilling due to generation of mechanical/thermal stress during a process. However, laser drilling barely generates mechanical/thermal stress on fabricated material. Thus, laser drilling is an effective tool for fabricating via holes on thin Si wafers.

In the mean time, monolithic interconnected thin film PV devices were proposed as an alternative of Si based PV devices due to increase of Si wafer cost. Copper-Indium-Gallium-Selenide (CIGS) thin film solar cell (TFSC) has been highly studied since it has high absorption coefficient for sunlight and relatively high theoretical efficiency limit
(-27%).[10, 11] CIGS thin film (1-2.5 µm)[12, 13] can be prepared by various methods that include sputtering, evaporating, ink-jet printing, etc. For mass production with low cost, ink-jet printing is preferred. However, it is difficult to fabricate the electric isolation lines for monolithic interconnection without delamination of ink-jet printed CIGS film due to low adhesion between ink-jet printed CIGS molecules. Two scribing techniques are currently applied for fabricating electric isolation lines on TFSC for monolithic interconnection: the mechanical scribing with stylus and the laser scribing. The mechanical scribing with stylus can enhance mechanical/thermal stress and cause delamination of layers. However, laser scribing can fabricate electric isolation lines without delamination since laser pulse does not inflict elsewhere except focal zone. Therefore, laser can be an efficient processing tool for fabricating electric isolation lines on ink-jet printed CIGS TFSC.

Nonlinear interaction of femtosecond laser pulse with materials opens up the possibility of interesting structures fabricated on wide band-gap semi-transparent dielectric materials. The interesting structures include nano-scale periodic structures on surface, three-dimensional structures in bulk, and etc. Laser induced periodic structures on surface (LIPSS) are often referred to as nano-ripples. Such structures were first found in semiconducting materials by Birnbaum on 1965.[14] LIPSS can be categorized by the width of period (Λ) such as low and high spatial frequency LIPSS. (LSFL and HSFL, respectively) The LSFL has Λ similar to wavelength (λ) or λ/2 and HSFL has Λ smaller than λ/2.[15] The origin of LSFL is clearly understood, while that of HSFL has been controversially discussed.[15] LSFL is generated by interference between irradiating laser pulses and surface electromagnetic wave (SEW).[16] On the other hand, HSFL may be generated by the effect of second harmonic generation (SHG),[17] specific types of plasmon,[18] and/or self-organization.[19] We fabricated HSFL on lithium niobate (LN) wafer surface by femtosecond laser for applying to two-dimensional photonic crystal. LN is human-made dielectric material that has electro-optical, acousto-optical, nonlinear optical, ferroelectric, photo-elastic, and photo-refractive properties.[20] Therefore, LN has high technical relevance and has been intensively studied in last few decades. Its band gap is 3.75 eV and hence equivalent to photon energy of 320 nm wavelength laser light. Meanwhile, most optics for processing systems consist of dielectric transparent materials and UV light can be absorbed by most dielectrics. To avoid a damage of optics, visible or IR light is preferred for laser processing. Thus, to fabricate LN, multiphoton absorption (MPA) of processing beam should occur within the focal zone. Therefore, femtosecond laser processing is an efficient tool for fabricating nano-scale structures on LN crystal surface.

On the other hand, nonlinear interaction can fabricate 3D structures in semi-transparent materials. The 3D structures may have various applications, but in the course of this work we focused on fabricating helical microchannel in fused silica for chemical/biological mixing. The mixing in the microchannel has been interested as a part of lab on a chip (LOC) device.[21-23] To enhance mixing without external energy input, transverse flow was generated via wedges on the channel floor.[24] Furthermore, enhancement of mixing rate can significantly reduce the length of mixing channel and it is preferred in LOC devices. Previous studies indicate that transverse flow can be effectively generated by 3D helical channel with circular cross-section.[25] Additionally, glass (fused silica) is an deal material for applying biological/chemical study due to its
strong resistance to various chemicals and transparency for visible lights. Therefore, 3D helical microchannel was fabricated in fused silica by femtosecond laser irradiation and chemical etching (FLICE) technique. The FLICE was first reported by Marcinkevicius et al.[26] It consists two steps: 1) waveguide writing in fused silica and 2) chemical etching of waveguide. Since it entails isotropic wet etching, circular channels can be fabricated. The waveguide writing was based on MPA since the band gap of fused silica is ~8 eV.[27] Therefore, it is possible to fabricate 3D waveguide in fused silica without inflicting elsewhere. Furthermore, the waveguide was etched by diluted hydrofluoric acid (HF) hence producing a 3D microchannel. To understand fluidic motion in helical channel, numerical analysis and experiments were performed.

In this dissertation, laser processing techniques that include femtosecond laser processing on thin and brittle Si wafer, thin and easily delaminated CIGS thin film, LN crystal, and fused silica were studied and the fabricated materials could be applied to PV devices, photonic crystal, and LOC devices. The following chapters will include more in detail about our studies.

Chapter 2: Before we discuss about previously listed laser processing techniques in detail, a brief introduction of laser processing is required. In this series of studies, we were focused on material removal (ablation or etching) process by femtosecond laser. Therefore, we will discuss about femtosecond laser ablation and related phenomena.

Chapter 3: Laser drilling on thin and brittle PV materials (crystalline and multicrystalline Si) was studied. The self-guiding of processing laser light that includes self-trapping and filamentation in ambient air was generated and it assisted to fabricate via holes in silicon wafers. To understand physical phenomena during laser drilling, scanning electron microscopy (SEM) images, emission images, and shadowgraph images were studied. The result indicates the existence of two mechanisms that include fabrication by self-guided beam and wall-guided beam. Based on our study, we could fabricate ~16 µm circular-shaped via holes with accumulation of ~200 laser pulses on 160-170 µm thick c- and mc-Si wafer.

Chapter 4: Laser scribing on ink jet printed CIGS TFSC was studied. The effects of wavelength, pulse accumulation, pulse energy, heat accumulation, and overlapping on laser scribing were elucidated via analyzing of SEM images. In the high PRF fs laser scribing, the effect of wavelength could be negligible while pulse accumulation was affective. On the other hand, the pulse accumulation could be negligible in the low PRF fs laser scribing. In the low PRF fs laser scribing, pulse energy affected to morphology of scribed lines. We revealed that the critical energy fluence initiating delamination of CIGS layer. To prevent a delamination and fabricate fine structure, overlapping was effective. Based on our study, the isolation line with ~1 µm could be fabricated.

Chapter 5: Femtosecond laser ablation of LN was studied. The ablation thresholds and LIPSS patterns according to the angle formed between laser polarization and crystal orientation were elucidated via SEM images. We could observe that the ablation threshold as well as LIPSS patterns were affected by the angle between laser polarization
and crystal orientation. Additionally, we could fabricate ~45 nm dot on z-cut LN wafer surface along the x-axis.

Chapter 6: 3D helical microchannel was fabricated in fused silica and applied to protein mixing. The channel was fabricated by FLICE technique with diameter of ~50 µm. For understanding of fluidic transport in the helical channel, numerical analysis was performed via COMSOL software. In the numerical analysis, we found the existence of the effective mixing condition due to compensation between the residence time of flow in the helix and the transverse patterns of flow. Our experiments supported the numerical analysis and we could achieve 90% mixing of Streptavidin-Alexa conjugate and deionized (DI) water within ~400 µm distance from confluence of two streams.

Chapter 7: Summarize and highlight this series of studies and provide a suggestion of future directions related with current works.
Chapter 2

Femtosecond laser ablation and related phenomena

2.1 Femtosecond laser ablation

High intensity of laser light can initiate an ablative material removal. Reference to “laser ablation” encompasses several mechanisms such as photothermal (or thermal), photochemical (or electronic), hydrodynamical, and exfoliational ablation mechanism. The photothermal ablation occurs via bond breaking of atoms by the lattice vibrational energy that is transferred from the energy of the irradiating laser light. In contrast, the photochemical ablation occurs via bond breaking of atoms by laser-induced electronic excitations. Both mechanisms enhance the liberation of atomic materials. On the other hand, hydrodynamical and exfoliational mechanisms enhance the liberation of bulk materials. The hydrodynamical ablation occurs via fluidic motion of micrometer scale droplets by laser-induced melting of material and the exfoliational ablation is mediated via separation of flakes from the surface by energy-absorbing defects.[1]

In femtosecond (fs) laser ablation, photochemical ablation process predominantly occurs since the pulse duration of fs laser is shorter than the electron-phonon relaxation time. (i.e. heat exchange between irradiating laser pulses and the material is barely occurred during the fs laser material interaction.) Therefore, we can diminish the thermal effect and fabricate precise structures on the material. Additionally, ablated damage fabricated by fs laser pulse is more regular than by longer pulses. Because of these characteristics, fs laser can be an effective tool for precise material processing.[1]

2.2 Nonlinear absorption in wide bandgap materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Bandgap (eV)</th>
<th>Wavelength (nm)</th>
<th>photon energy (eV)</th>
<th>Number of photons (m)</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3.85</td>
<td>800</td>
<td>1.50</td>
<td>3</td>
<td>MPA</td>
</tr>
<tr>
<td>CIGS</td>
<td>1.2-1.7</td>
<td>1043</td>
<td>1.15</td>
<td>2</td>
<td>TPA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>1.50</td>
<td>1-2</td>
<td>SPA, TPA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>522</td>
<td>2.30</td>
<td>1</td>
<td>SPA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>3.00</td>
<td>1</td>
<td>SPA</td>
</tr>
<tr>
<td>LiNbO3</td>
<td>3.75</td>
<td>400</td>
<td>3.00</td>
<td>2</td>
<td>TPA</td>
</tr>
<tr>
<td>Fused silica</td>
<td>8</td>
<td>522</td>
<td>2.30</td>
<td>4</td>
<td>MPA</td>
</tr>
</tbody>
</table>

Table 2-1. Classification of absorption mechanism in this dissertation. (SPA: single-photon absorption, TPA: two-photon absorption, and MPA: multi-photon absorption)

In semiconducting and dielectric materials with wide bandgap, irradiation of high intensity (10^{11} \sim 10^{14} \text{W/cm}^2) laser-light enhances the absorption of laser pulse energy via nonlinear ionization mechanisms that include multi-photon ionization, tunneling
ionization, and avalanche ionization. The bandgap of tested materials are listed in table 2-1. Note that for Si, direct bandgap (3.75 eV) should be considered since the absorption via indirect bandgap requires the assistance of lattice vibration. (figure 2-1. (a))

2.2.1 Multi-photon absorption

Figure 2-1 (b) depicts the single- and multi-photon absorption. Single-photon absorption occurs when the photon energy \((\hbar \omega)\) of irradiating laser pulse is bigger than bandgap \((E_g)\) of material and multi-photon absorption occurs when the photon energy of irradiating laser pulse is smaller than bandgap. In contrast to single-photon absorption that is spontaneous, extremely high intensity (~ 1 GW/cm²) of laser light should be irradiated to initiate multi-photon absorption.[28] The rate of multi-photon absorption can be expressed as following equation:[1]

\[
P(I)_{MPA} = \sigma^{(m)} I^m
\]

where \(\sigma^{(m)}\) is the cross section of \(m\)-photon absorption (a probability of simultaneous absorption of \(m\) photons), \(I\) is the laser intensity, and \(m\) is the smallest number of photon to satisfy the relation \(m(\hbar \omega) > E_g\).

![Figure 2-1. (a) Direct and indirect bandgap of silicon. In fs laser processing, direct bandgap should be considered. (b) Single and multiphoton absorption. \((E_g\) indicates a bandgap of material and \(\hbar \omega\) indicates photon energy of laser pulse)]
2.2.2 Tunneling ionization and Keldysh parameter

The tunneling ionization can be enhanced under extremely intense fs laser irradiation. In this regime, the laser pulse energy induces periodic band-bending (or distortion of binding atomic potential), which allows direct tunneling of electrons from valence band to conduction band.[1] (figure 2-2. (a)) In 1965, Keldysh suggested a parameter (Keldysh parameter) that can express both regimes of the multiphoton and tunneling ionization with adiabatic parameters.[29]

\[
\gamma_{Ke} = \frac{\omega \sqrt{2m_e E_g}}{eE}
\]  

where \(\omega\) is the angular frequency of laser light, \(m_e\) is the effective mass of electron, \(e\) is charge of electron, and \(E\) is the intensity of electric field oscillating at frequency \(\omega\). When the Keldysh parameter is grater than 1.5 (\(\gamma_{Ke} > 1.5\)), multi-photon ionization dominantly occurs and the Keldysh parameter is smaller than 1.5 (\(\gamma_{Ke} < 1.5\)), tunneling dominantly occurs. If the Keldysh parameter is around 1.5 (\(\gamma_{Ke} \sim 1.5\)), the multiphoton absorption occurs followed by tunneling ionization.

Figure 2-2. (a) Tunneling ionization. Upper schematic shows the natural behavior of atoms and lower schematic shows the tunneling ionization initiated by laser-induced distortion of binding atomic potential. (b) Avalanche ionization. Left hand side schematic shows the absorption of irradiating laser energy by excited electrons and right hand side schematic shows the kinetic energy transfer from excited electrons to valance band electrons. Where \(E_c\) is the kinetic energy of excited electrons in conduction band.
2.2.3 Avalanche ionization

After electrons are excited from valance band to conduction band, excited electrons can linearly absorb the laser irradiations like a metal. As a result, the electrons experience the intra-band transitions within the conduction band. The kinetic energy of the intra-band transited electrons can be transferred to electrons in valence band. If the transferred energy is greater than bandgap of material, the electrons are excited to conduction band. (figure 2-2 (b)) Reference to “Avalanche ionization” rapidly increases the number of electrons in conduction band. To initiate the avalanche ionization, “seed electrons” should be present in conduction band. The following equation describes the excitation of electrons from valance band to conduction band via avalanche ionization:[30]

\[
\frac{dN}{dt} = \beta_{av} N = \alpha_{av} IN
\]

(2.3)

where \(N\) is electron density, \(\beta_{av}\) is the avalanche ionization rate, and \(\alpha_{av}\) is constant. Combining with multi-photon ionization, above equation can be extended as:[1]

\[
\frac{dN}{dt} = \alpha_{av} IN + \sigma^{(m)}Nl^m
\]

(2.4)

Note that electron population in conduction band depends on laser intensity \((I)\).

2.3 Ablation threshold of materials

The fs laser processing induces regular structures on materials due to aforementioned characteristics. Therefore, if the processing parameters for obtaining a specific structure are provided, it can be reproduced elsewhere. In most instances, the pulse energy fluence \((J/cm^2)\) is presented for that purpose. There is a minimum fluence to initiate the material removal (ablation). Reference to “Ablation threshold” is indeed a useful parameter for laser processing. The ablation threshold of material \((F_{th})\) and Gaussian beam waist \((\omega_0)\) can be determined from relation between the square of ablated crater diameter \((D^2)\) and logarithm of pulse energy fluence \((\ln F)\). This can be expressed as following equation:[31, 32]

\[
D^2 = 2\omega_0^2 \ln \left( \frac{F_0}{F_{th}} \right)
\]

(2.5)

For the multi-photon absorption and relatively high pulse energy fluence, the effective penetration depth should be considered to determine the ablation threshold of material:[33]

\[
x_{abl} \approx l \times \ln \left( \frac{F}{F_{th}} \right)
\]

(2.6)

where \(x_{abl}\) is the depth of ablated crater and \(l\) is the effective penetration depth. Previous research studies indicate that the effective penetration depth can be affected by intensity
of laser pulse.\[33, 34] The ablation threshold can be a guideline for attempting to fabricate new structures on the material and useful parameter for understanding (as well as comparing) various materials.

2.4 Self-actions of light in wide bandgap material

The propagation of intense laser light in wide bandgap material induces microscopic displacement of bound charges. This displacement forms an oscillating of electric dipoles and the polarization at the frequency of the incident laser field. The refractive index of material accounting this nonlinear interaction can be represented as following equation:

\[ n = n_0 + n_2 I \]  \hspace{1cm} (2.7)

where \( n_0 \) is linear refractive index and \( n_2 \) is nonlinear refractive index. Since the values of \( n_2 \) are very low (for example, \( n_2 \) for Si is \( 2.7 \times 10^{-14} \text{ cm}^2/\text{W} \), \( n_2 \) for fused silica is \( 3.2 \times 10^{-16} \text{ cm}^2/\text{W} \), and \( n_2 \) for air is \( 5.0 \times 10^{-19} \text{ cm}^2/\text{W} \)\[35\]), intense laser pulses should be irradiated to enhance a nonlinear contribution \( (n_2 I) \) in refractive index of material.

Irradiation of a Gaussian beam can generate spatially varying refractive index in wide bandgap materials. In the Gaussian beam, the intensity along the center axis is higher than that of the periphery. Hence, the beam center experiences larger refractive index than the periphery when the nonlinear refractive index is positive. As a result, the material acts as a focusing lens. (Figure 2-3. (a))

However, the electron density at the focus does not infinitely increase. When the nonlinear mechanisms that include multi-photon absorption and self-focusing effect generate electron-hole plasma at the focus, modification of the refractive index occurs. Adjusting to this change, the light diverges, i.e. the so-called plasma defocusing. (Figure 2-3 (a)) The refractive index modification due to electron-hole plasma can be described as following equation:\[36]\n
\[ n = n_0 - \frac{N}{2n_0 N_c} \]  \hspace{1cm} (2.8)

where \( N_c \) is the characteristic plasma density when the plasma frequency is equal to the laser frequency:

\[ N_c = \frac{\omega^2 \epsilon_0 m_e}{e^2} \]  \hspace{1cm} (2.9)

The balance between self-focusing and plasma defocusing creates self-trapping or filamentation of light in the material. Figure 2-3 (b) depicts the self-trapping of light in a wide bandgap material. The exact balance between self-focusing and plasma defocusing elongates the depth of focus. The critical power for creating self-trapping can be determined by following equation\[35\]:

\[ P_{cr} = \frac{\pi(0.61)^2 \lambda_0^2}{8n_0 n_2} \]  \hspace{1cm} (2.10)
where $\lambda_0$ is the wavelength of light in vacuum. If the power of the irradiating laser pulse exceeds the critical power, laser light can break up into several narrow filaments, i.e. the so-called filamentation. (figure 2-3 (c)) In chapter 3, we generate filamentation in the air. The experimental result indicates that elongation of laser light was observed at 25 $\mu$J and higher. (figure 3-2) The estimated critical power of ambient air (equation 2.10) is ~1.87 GW.

Figure 2-3. Self-actions of light in wide bandgap materials. (a) Self-focusing and plasma defocusing, (b) Self-trapping, (c) Filamentation
Part 1

Photovoltaic materials

Chapter 3

Femtosecond laser drilling of mc-Si and c-Si for wrap through solar cells

3.1 Introduction

In order for photovoltaic power generation to be a viable solution to the global energy challenge, it is critical to increase the solar cell efficiency. One possible route to this end is to increase the amount of sunlight that reaches the photo-conversion layer. In conventional solar cells, front electrodes collect generated electrons. However, the front electrodes cast shadow underneath, the so-called shading effect, consequently reducing the overall efficiency of solar cell. In order to overcome this limit, metal wrap through (MWT) or emitter wrap through (EWT) design has been suggested by shifting top contact to rear through via-holes. [4] MWT effectively replaces the front electrode by via holes, typically requiring ~ 10,000 via holes in one panel (154 mm × 154 mm) for sufficient carrier transport. The other approach, emitter wrap through (EWT), needs even higher density of holes; ~ 25,000 via holes in one panel since the via holes are filled with emitters rather than metal. [5] Definitely, via-holes of higher aspect ratio and small diameter are preferred considering the goal of reducing the shadow area on the front surface and increasing the exposed volume. In this context, one can expect that ultrashort pulsed laser may be favorable, taking advantage of minimal lateral thermal diffusion and indeed sub-10 µm via hole diameter was reported in a 250 µm thick single crystalline silicon (c-Si) wafer with femtosecond laser at ~1300 laser shots (repetition rate: 13 MHz, dwell time: 100 µs). [37]

While the theoretical efficiency of c-Si based solar cell can reach ~29%, [6] multi crystalline silicon (mc-Si) is also of great interest as base material due to its merit in the material cost. It is noted that in 2004, O. Schultz et al. recorded 20.3% efficiency with a 99 µm-thick mc-Si solar cell. [7] The wafer thickness is determined by compensating between the absorption depth of the solar spectrum and the diffusion length of minority carriers. The absorption depth at AM1.5G (λ ≤ 1100 nm) is ~3.7 mm. [38] However, even though electron-hole pairs are generated by absorption, minority carriers should reach the edge of depletion region to generate current. The diffusion length of electrons in p-type doped c-Si is ~ 200 µm at the acceptor concentration of ~10^{17} cm^{-3} [8] while it
decreases as the doping concentration increases. However, lower concentration of acceptors generates lower minority carriers in the photo-conversion layer. In this manner, \(10^{17} \text{ cm}^{-3}\) is a well-accepted value for solar cell. For mc-Si, the measured diffusion length of minority carriers is \(\sim 80 \mu \text{m}\) [9] due to faster recombination of minority carriers at grain boundaries or defects. Therefore, \(\sim 200 \mu \text{m}\) is selected as reasonable maximum thickness of the wafer and accordingly selected for this study. However, thickness of \(\sim 200 \mu \text{m}\) still poses challenges to drill a high density via holes at reasonable manufacturing cost and speed with conventional methods, in particular, for fragile mc-Si wafers. Thus, laser drilling has been considered as alternative non-contact via-hole fabrication method. Previous studies demonstrated the via hole drilling processes based on nanosecond [39-41], picosecond [42], and femtosecond [37, 43-48] lasers. However, systematic studies on mc-Si drilling by ultrafast lasers are rare.

As mentioned earlier, femtosecond laser is favorable for high-aspect ratio via-hole fabrication. However, previous research has shown that over 1,000 shots are required to drill via holes in a silicon wafer of thickness 200 ~ 250 µm. [42, 46, 47] This yield needs to be improved to meet the processing speed demand. In order to optimize the process speed, the physical mechanisms at higher pulse energy conditions must be carefully examined.

It should be noted that non-linear self-guiding effect that includes self-trapping and filamentation is more prominent at higher pulse energy regime. Because a Gaussian beam is commonly used in this process, the center region carries a higher flux of photons than the periphery. In the non-linear regime, the refractive index is not constant but varies as a function of the local laser intensity in a homogeneous medium irradiated by a femtosecond laser beam. (equation 2.7) Therefore, the refractive index is higher at the center than the perimeter of a Gaussian laser beam, thereby inducing self-focusing. [49] (figure 2-3 (a)) On the other hand, high peak intensity may generate plasma at the center that causes defocusing. (figure 2-3 (a)) The dynamic balance between self-focusing and plasma defocusing produces self-guiding, significantly increasing the effective depth of focus (DF) compared to the linear regime. [35, 50] (figure 2-3 (b), (c)) We attempt in this work to utilize the extended effective DF by the self-guiding effect in order to achieve high aspect ratio holes and reduce the total number of shots to drill a via hole. Even though, the objective lens that has longer DF in linear regime is preferred. The DF in linear regime is inverse proportional to a square of numerical aperture (NA\(^2\)), and beam size is inverse proportional to numerical aperture (NA). To fabricate via holes for advanced solar cell, relatively small hole is preferred. To solve a conflict between longer DF and smaller hole size, several settings with various NAs are tested. After testing objective lenses of several different NA settings, an objective lens of 0.14 NA was chosen within range of laser pulse energy tested in this study at selected focal condition; the self-guiding occurs in the ambient air and the effective DF is extended to be comparable with the target drilling thickness of Si wafers, and the effective laser focal spot is the order of 10 µm. The extension of DF by self-guiding effect can prevent significant attenuation of energy density in the axial direction as drilling progresses and consequently contributes to the reduction of the number of shots to drill via holes. In near infrared (NIR) femtosecond laser processing, absorption is decoupled from phonon emission. Therefore, electronic transition through indirect bandgap (~1.12 eV) [50] is irrelevant and instead absorption occurs across the direct band gap of ~3.375 eV via a
multi-photon process. [34, 51] (figure 2-1) Hence, the effective penetration depths in c-Si and mc-Si need to be considered as these affect the ablation depth in the case of a multi-photon laser ablation process.

The main practical objective of this work is to reduce the required number of laser shots and hence increase processing speed for via-hole drilling through parametric studies of the pulse energy and the relative sample position with respect to the extended laser focal region, for both c-Si and mc-Si wafers. We also conduct a detailed study to understand the physical phenomena that occur during the drilling process by cross sectional analysis, as well as by plasma emission and time-resolved shadowgraph imaging analysis.

3.2 Experimental

3.2.1 Femtosecond laser drilling

A Ti:Sapphire femtosecond laser (\(\lambda = 800\) nm, \(\tau = \sim 80\) fs, Spectra Physics Spitfire) is used for this study. Figure 3-1 shows a schematic diagram of the experimental set up. A 5X objective lens (NA 0.14, DF at linear regime of \(\sim 14\) µm, Mitutoyo) is used to focus

![Figure 3-1. A schematic diagram of the femtosecond laser drilling and observation](image-url)
the processing laser beam and the triggering of laser is controlled via a delay generator (Stanford Research Systems). The beam diameter is ~13 µm ($1/e^2$) as measured by a knife-edge method at low laser pulse energies in linear regime.

However, it should be noted that once self-focusing and self-guiding take place, the beam diameter tends to decrease and the effective DF increases. To observe this trend, side view images are taken by a CCD camera as shown in figure 3-2(a) for ~50 µJ pulse energy without sample. In the figure, rough beam trajectory is visualized via plasma emission. The plasma emission is a result of air breakdown occurring near the focal zone when the local intensity exceeds the respective threshold. [34] The length of the emitting

![Figure 3-2. (a) Side view image of generated air plasma 50 µJ case; circle in the figure 3-2(a). (b) Air plasma length without sample; repetition rate: 100 Hz, objective lens: 5X (NA 0.14, linear DF: 14 µm)]
plasma for different pulse energy applied is plotted in Figure 3-2(b), demonstrating the increasing trend of the effective DF in the nonlinear regime. The laser pulse energy is carefully measured at a location between the lens and the laser focus (position M on the figure 3-1); before the nonlinear regime commences. At the laser pulse energy of ~50 µJ, the length of the extended focal zone caused by nonlinear effects is at least 90 µm. When the energy is increased, the location of the forward air plasma tip changes relatively little compared with overall plasma length. Thus, we set this point as the reference zero position. In order to explore the more precise effect of the nonlinear beam propagation on drilling, 5 different fixed sample positions (60 µm, 30 µm, 0, -30 µm, -60 µm) are selected in actual drilling test. The positive and negative signs indicate that the sample is positioned farther away and closer to the lens, respectively.

3.2.3 Cross-sectional analysis

Scanning electron microscope (SEM) is used to characterize the morphology of the sidewall surface. For cross-sectional analysis, we have to cut across the drilled holes by combining scribing and drilling. First, a 1 mm long line is scribed on a sample surface by laser pulses at 50 µJ pulse energy at 1000 Hz pulse repetition frequency, scanning three times at the speed of 0.2 mm/s. After checking the spatial extent of heat- & shock-affected zone multiple times (typically less than 100-150 µm at the given drilling conditions), starting at a 300 µm from one end of this scribed line, seven craters are drilled at 100-150 µm interval with 10 to 70 shots at 50 µJ and 20 Hz. After the hole drilling, another 1 mm long line is scribed the same way. Repetition of this scribing-drilling combination realizes a guideline for severing the sample with pliers.

3.2.4 Time resolved study of shock wave propagation

Figure 3-1 also shows the time-resolved imaging set up for capturing the propagation of shock wave that is generated during the drilling process. A nitrogen laser pumped dye laser beam (l = 440 nm, t = 10 ns, Laser science Inc.) is used as illumination light source and is controlled by a delay generator (Stanford Research Systems). The actual time delay is measured with two photodetectors (Thorlabs) and an oscilloscope (LeCroy 9354AL). A 5X objective lens (Olympus) is used for side view observation: emission and shock propagation. After the objective lens, Notch filters (center wavelength = 808nm, bandwidth = 41 nm) are placed to block the processing (λ = 800 nm) laser light.

3.3 Result and discussion

3.3.1 Number of shots

The goal of this research is to identify a process condition that minimizes the total number of laser shots required to drill via holes of ~20 µm diameter. To reduce the
number of shots, two process variables are considered: pulse energy and relative sample position with respect to the nonlinear laser focal region. One may anticipate that increasing the energy would simply reduce the number of shots. However, the actual experimental trend was more complex than expected as will be explained in detail. As seen in Figure 3-2 (b), air breakdown and self-guiding are enhanced as the energy is increased, extending the focal zone in the light propagating direction. Figure 3-3 depicts the relationship between the applied pulse energy and the minimum numbers of shots for drilling through at different sample placement positions. A He-Ne continuous-wave laser beam (λ = 633 nm) illuminates the backside the target specimen, where transmission of the He-Ne laser light verifies the completion of a through hole. Both at 60 µm and 30 µm sample positions, the minimum number of shots to complete drilling on a c-Si wafer does not change significantly within the applied energy range (40 µJ ~ 80 µJ). However, when the sample is moved closer to the lens (-30 µm and -60 µm), the minimum number of shots required to complete drilling is significantly reduced (Figure 3-3 (a)). A similar tendency is identified in Figure 3-3(b) for mc-Si. The results imply that if we apply self-guided beam to the sample, the magnitude of irradiated energy will be maintained as the drilling proceeds through the sample upon proper adjustment of sample position respect to the elongated focal region (i.e. located the extended focal region within sample to be drilled through).

Figure 3-4 depicts the relative location of sample with respect to the nonlinearly formed plasma (z indicates the sample location). To verify this hypothesis at early stage of the drilling process, side view emission images have been acquired for different sample locations (Figure 3-4. (a) for c-Si and (b) for mc-Si, overlapped images for first ~3 pulses at 100Hz). Compared to air plasma emission without sample, enhancement in overall plasma emission intensity with sample is due to emitted electrons originated from silicon surface. [34, 52, 53] On top of the surface electron initiated air plasma, additional emission components induced by material ejection are distinct in the images, clearly showing that sample placement closer to the laser focal region leads to more vigorous material ablation. Interestingly, even though the sample is moved towards the lens, the
starting location of the air plasma is roughly the same implying that a larger fraction of the laser energy is utilized for actual drilling.

Similarly, the shadowgraphs taken at about 100 ns after the femtosecond beam (figure 3-4(c), single laser shot induced shock images with fresh sample surface of c-Si) show that expansion of the ablation-induced shock wave is relatively faster for samples located closer to the lens and consequently more energy is delivered to the ablated ejecta. As prominent difference between c-Si and mc-Si ablation, material ejecta from a mc-Si sample drilling spot is more vigorous at wider spreading angles. (Figure 3-4 (a) and (b))

3.3.2 Cross-sectional study

Figure 3-5 shows cross-sectional scanning electron microscopy (SEM) images of c-Si and mc-Si samples drilled by laser pulses of ~50 µJ energy with the samples located at the zero reference position. The ablation depth is measured by the SEM length measurement tool.
For multi-photon absorption, the effective penetration depth has to be considered. Hwang et al. (2006) confirm that the femtosecond laser-induced ablation depth per single pulse of c-Si with respect to the applied fluence follows the relationship: 

\[ x_{\text{abl}} = 322 \times \ln\left(\frac{F}{0.637}\right) \]

where 322 nm is the effective penetration depth, 0.637 J/cm\(^2\) is the ablation threshold of c-Si, and \( F \) is applied energy fluence. We have verified similar values for c-Si based on current experimental conditions, and also measured the ablation depth of mc-Si as a function of the laser fluence by single shot experiments, as shown in Figure 3-6. For mc-Si, we can establish the following relationship: 

\[ x_{\text{abl}} = 319 \times \ln\left(\frac{F}{0.425}\right) \]

where 319 nm is the effective penetration depth, 0.425 J/cm\(^2\) is the ablation threshold of mc-Si. (Figure 3-6) According to Basore et al. (1994) the mc-Si grain size is in the range of 1 µm to 10 cm. Accordingly, one may anticipate that both the effective penetration depth and the ablation threshold for mc-Si exceed the respective
values of amorphous silicon (a-Si) but should be lower than those of c-Si. Indeed, the ablation threshold of a-Si is 0.32 J/cm$^2$. [55]

The ablation depth data presented in Figure 3-7 identify two distinctive linear ablation rate regimes. Initially, the ablation rates are higher, with fitted value of 790 nm/shot and 990 nm/shot for c-Si and mc-Si, respectively. The higher ablation rate occurs at 0 ~ 120-130 µm depth from the surface. The relatively lower ablation depth rate occurs after the depth exceeds about 130 µm; 370 nm/shot and 740 nm/shot for c-Si and mc-Si, respectively. Obviously, this trend is closely related to the complex beam propagation in nonlinear regime such as self-guiding effect, and further details are discussed in the next section.

3.3.3 Self-guiding effect verification with changing sample positions

To better understand self-guiding effects on the complex mechanisms of c-Si and mc-Si drilling, we have changed the sample placement to 50 µm. The ablation (drilling) depth variation for this placement is overlapped on data corresponding to the zero sample placement in Figure 3-7. The abrupt change in ablation rate for the 50 mm position occurs at a depth of ~80 µm, while for the zero placement is observed at ~120-130 µm. The relative difference in the transition placement of ~40-50 µm approximately matches the difference in the sample location (+50 µm; out of sample), thereby confirming the favorable effect of elongated effective DF.

For further detailed investigation of two distinct ablation rate regimes, from the SEM images inserted in Fig. 3-7, we find that the overall drilling hole shape is clearly tapered.
and the tip of a hole is round and pointed in the lower drilling rate regime (i.e. deeper holes; deeper than the transition position) while relatively uniform in drilled diameter and flat ended for higher drilling rate regime (i.e. shallower holes; shallower than the transition position). Since the laser beam has Gaussian shape, a pointed tip would be expected. However, a different, non-Gaussian beam intensity profile in higher drilling regime (where sufficiently high local laser intensity is still maintained) would be expected in the presence of nonlinear effects. [56] Thus, we can conclude that there are two different mechanisms to drill silicon: self-guided beam ablation (direct focusing) and wall guided beam ablation (indirect focusing). In the second regime (lower drilling rate, wall guided), the tapered drilling hole implies significant reduction in the guided laser intensity at the hole.

It is noted that the overall ablation rate is much faster and the change in ablation rate less prominent in mc-Si drilling. This trend is mainly attributed to the structure of mc-Si and represented in the lower ablation threshold (Figure 3-6) as well as the splash-like ablated ejecta trajectory (Figure 3-4(b)). Under complex plasma evolution within the confined domain of the pre-drilled hole, the femtosecond laser induced air plasma explosion [52] may generate an additional driving force for the mc-Si material removal. Almost single linear drilling regime (i.e. almost linear between number of laser shots and drilling depth) for given target drilling depth is practically advantageous in terms of drilling depth prediction. Also, the existence of a linear regime up to ~120-130 µm for c-Si will be useful for thinner c-Si solar cell design that maybe realized via technical advance (e.g. enhanced light trapping).

3.3.4 Effect of femtosecond laser induced plasma formation

Mao et al. (2000) [53] reported surface electron initiated air plasma formation via the photoelectric effect and collision with surround air molecules upon ultrashort laser pulse irradiation. The surface electron initiated air plasma formation has been experimentally verified for silicon sample by femtosecond laser of 800nm wavelength at laser energy densities far below direct air breakdown threshold (\(<<~50\,\text{J/cm}^2\)) [34].

Figure 3-8 shows the ablated crater entrance area of both c-Si and mc-Si as a function of the energy fluence. The dotted line indicates the energy that air plasma starts to be formed. Once air plasma occurs, the ablated area increases rapidly (Figure 3-8). Ellipsoidal crater opening shape is observed below the air plasma formation threshold, and circular upon the air plasma formation. Venkatakrishnan et al. (2002) reported the effect of polarization when a thin film is ablated by ultrafast pulsed laser. [57] They used 150 fs laser pulse and found that the shape of the ablated hole exhibits a shape indicative of the polarization direction. Thus, to obtain a circular shaped hole, circularly polarized beam would be preferred. When the air plasma is formed, the polarization effect is diminished as a shock wave is released, exerting a recoil pressure on the surface and facilitating debris removal. This explains the circular hole shape obtained in this study, independent of the laser polarization in the high pulse energy regime. Figures 3-9 (a) and (b) shows the entrance and exit of fabricated hole at high pulse energy regime (80 µJ, 180 pulses, mc-Si).
Figure 3-8. Ablated area of c-Si and mc-Si by applied laser energy fluence; Single pulse on the fresh surface and air plasma is formed after 25 µJ (dotted line indicates it)

Figure 3-9. Circular entrance and exit fabricated at high energy regime; 80 µJ, 180 pulses, mc-Si. (scale bar indicates 10 µm), (a) Entrance (close to laser incoming), (b) Exit (opposite side with laser incoming)
Through the shadowgraphs presented in Figure 3-10, we can verify that the shock wave initiated by the air breakdown collides with the shock wave emitted from the surface at a time less 10 ns after the irradiation of the laser shot. Traditional models, including the blast wave model [58] and the drag force model [59], are certainly insufficient for explaining these phenomena and quantifying the pressure exerted on the surface. The shadowgraphs reveal that the ablation shock wave speed and radius are somewhat faster and larger for mc-Si compared to c-Si. This implies that the blast energy triggering the shock wave release is larger for mc-Si than for c-Si, consistent with the respective faster ablation rate. In terms of detailed structure, the shock waves emitted from mc-Si appear irregular and perturbed, likely because of the enhanced fragmentation and irregular disintegration of the target.

Figure 3-10. (a) Time resolved images of shadowgraphs (c-Si); single pulse on the fresh surface, laser pulse energy: 50 µJ, and each time on the frame indicates the time delay., (b) Time resolved images of shadowgraphs (mc-Si); single pulse on the fresh surface, laser pulse energy: 50 µJ, and each time on the frame indicates the time delay.
3.4 Conclusion

(a) Time resolved images of shadowgraphs (c-Si); single pulse on the fresh surface, laser pulse energy: 50 µJ, and each time on the frame indicates the time delay. (b) Time resolved images of shadowgraphs (mc-Si); single pulse on the fresh surface, laser pulse energy: 50 µJ, and each time on the frame indicates the time delay. In this work, we aimed at reducing the total number of laser shots to complete ~ 20 µm diameter via holes in the mc-Si and c-Si sample. These via holes can be used as current paths for advanced solar cell configurations such as MWT and EWT. The propagation of the ultrafast laser beam and its dynamic focusing were modified by the nonlinear interaction with the ambient air. As a result, the ablation efficiency depends on the applied laser fluence and the position of the sample respective to the complex nonlinear focal region. To understand this complicated drilling process, we carried out cross sectional analysis and side view observation via time resolved emission and shadowgraph imaging. Through cross sectional analysis, we found two distinct ablation mechanisms during the drilling process; (1) dominated by the direct self-guided beam at early stage, and (2) governed by the drilled cavity wall-guided beam at subsequent stage. In the wall-guided regime, significant reduction in the ablation rate was measured for c-Si. However, mc-Si showed higher drilling rate at similar laser pulse energy due to intrinsically weaker structure and stronger laser absorption. Future investigations will have to address the influence of various laser factors such as the wavelength, the repetition rate, and pulse duration.
Chapter 4

Femtosecond laser scribing of monolithic integrated CIGS thin film solar cell

4.1. Introduction

The photovoltaic (PV) devices have been interested in the last few decades as a renewable energy source that is an alternative of fossil fuels. One of the most important parameter for the PV devices is a production cost (cost per peak watt, $/W_p). To reduce a production cost, the device efficiency should approach theoretical limit and device cost (includes fabrication and material cost) should be reduced. As aforementioned in the chapter 3, the theoretical limit of silicon-based solar cell can reach up to 29%. [6] However, the price of single crystalline Si (c-Si) wafer keeps increasing as a corollary of growth of the semiconductor industry. For c-Si PV device, wafer cost constitutes about 60% of the PV device cost. [60] Therefore, alternative PV devices rather than Si based PV devices have been investigating. [61]

CuIn_xGa_(1-x)Se_2 (CIGS) thin film solar cell (TFSC) is one of a strong candidate as a next generation PV devices. A typical thickness of CIGS thin film is 1~2.5 μm, thus it may cost less than Si based PV devices that generate the same power. [12, 13] CIGS thin film can be prepared by various methods: co-evaporation, reactive sputtering of Cu, In, and Ga with Se, selenization and/or sulfurization of sputter-deposited Cu-In-Ga precursor, and selenization and/or sulfurization of Cu-In-Ga precursors by non-vacuum methods (electro-deposition, doctor-blade, and inkjet printing). [62] Even though the theoretical limit is under investigation [63], the efficiency of CIGS PV devices may reach up to 27%. [10, 11] CIGS PV devices have been demonstrated to be 20.3% efficient at the cell level (0.5 cm² cells) by the Zentrum für Sonnenenergie und Wasserstoff-Forschung Baden-Württemberg (ZSW), Germany. [64] Using an ink-based manufacturing process, cell efficiencies are much lower (~13% AM1.5) than the champion efficiency, but module fabrication costs are significantly reduced relative to processes that rely on vacuum-based deposition methods. Therefore, an ink-based CIGS TFSC was used in this work.

For terrestrial applications, monolithic interconnection of CIGS PV module is preferred. To achieve monolithic interconnection of CIGS sub-cells, several scribing processes are required: P1 (isolation of molybdenum back contact layer), P2 (isolation of CIGS active layer), P3 (isolation of CIGS active layer and transparent conducting oxide (TCO) layer), and P4 (isolation of entire layers at edge of device). Figure 4-1 depicts a monolithic integrated CIGS TFSC and related scribing processes. Since scribed lines form a dead zone that cannot generate free carriers in the CIGS active layer, thin scribed lines with a small gap are preferred in order to increase the device efficiency. Therefore, pulsed laser scribing has been applied to P1, P2, P3, and P4 process due to capability for fabricating thinner line than mechanical stylus scribing.
Compaan et al. has previously reviewed laser scribing of a wide variety of thin-film PV devices, including CIGS TFSC. [65] Progress toward damage-free laser scribing of CIGS cells has been recently reported with nanosecond (ns) pulses, [66] picosecond (ps) pulses, [67-70] and femtosecond (fs) pulses. [70, 71] However, fs laser scribing on an ink-based CIGS TFSC has not been investigated. Therefore, we studied various phenomena during fabrication of isolation lines by amplified fs laser and high repetition rate fs laser via morphology analysis that was performed by scanning electron microscope (SEM) and focused ion beam (FIB) cross-sectioning.

4.2 Experimental

4.2.1 Ink-based CIGS thin film solar cell

CIGS TFSC on glass substrates was fabricated using an ink-based process similar to the one that has been reported previously. [12, 13] Briefly, a ~0.5 µm thick molybdenum layer is sputter-deposited onto a glass substrate. An ink made of precursor nanoparticles of Cu, In and Ga oxides is then applied to the surfaces to generate an active layer with a thickness of 10-15 µm. This ink is reduced under hydrogen ambient, then annealed under H₂Se gas to achieve a final thickness in the range 1.2-1.5 µm. A thin CdS layer is formed by chemical bath deposition, followed by a transparent conducting ZnO layer applied with Low Pressure Organometallic Vapor Deposition (LPOVD). A finished TFSC is shown in Figure 4-2, after cross-sectioning by FIB to allow visualization of the various layers. Note that CdS layer between ZnO and CIGS layers is barely observed since the thickness of CdS layer is ~ 500 Å. Furthermore, the low adhesion of ink-jet printed CIGS layer can be observed. The delamination inside a CIGS layer may be generated by irradiation of FIB.
Yb-doped fiber based fs laser ($\lambda$: 1045 nm, $\tau$: ~400 fs, pulse repetition frequency (PRF): 100 and 1000 kHz, FCPA µJewel D-400, IMRA America, Inc.) and Ti:Sapphire fs laser ($\lambda$: 800 nm, $\tau$: ~100 fs, PRF = 1 kHz, Spectra Physics Spitfire) were used for this work. To elucidate the effect of wavelength, frequency doubling was achieved via second harmonic generation (SHG). Lithium triborate (LBO) second harmonic nonlinear crystal (Newlight Photonics) was utilized for frequency doubling of 1043 nm wavelength (IR) pulses and $\beta$-barium borate (BBO) nonlinear crystal was utilized for frequency doubling of 800 nm wavelength (NIR) pulses. As a result, 522 nm wavelength (VIS) pulses and 400 nm wavelength (NUV) pulses could be applied to the CIGS TFSC. The laser pulse energy was manipulated by combining a half-wave plate and a polarization beam splitter (PBS). Both power meter (for laser pulses with high PRF such as 100 and 1000 kHz) and energy meter (for low PRF, 1kHz) were applied for measuring pulse energies. The Yb-doped fiber based fs laser pulse was tightly focused via high magnification objective lens (50X, NA 0.55, Mitutoyo) and the Ti:Sapphire fs laser pulse was focused via low magnification objective lens (10X, NA 0.28, Mitutoyo) for irradiating similar energy fluence on the CIGS solar cell surface. For further reduction of the laser beam size, high NA objective lens (100X, NA 0.8, 100X) was adopted on VIS pulses of Yb-doped based fs laser. For the laser scribing of CIGS TFSC, precise motorized stages (X, Y axis, Newport PM500 series, 100 nm resolution) translated the sample with various speeds (0.01, 0.02, 0.05, 0.1, and 0.2 mm/s)
4.3 Result and discussion

4.3.1 Yb-doped fiber based femtosecond laser scribing on CIGS thin film solar cell

In a first series of experiments, we examined the effects of pulse accumulation (total number of pulses irradiated on the same site) and wavelength on the morphology of isolation lines fabricated by high PRF fs laser. In this study, pulse accumulation was determined by considering the beam waist and the scribing speed. Examined scribing speeds (0.01, 0.02, and 0.05 mm/s) were equivalent to accumulation of $\sim 3.8 \times 10^5$, $\sim 7.6 \times 10^5$, and $\sim 1.9 \times 10^6$ pulses, respectively. To elucidate the effect of wavelength, frequency doubled laser pulses were generated via SHG. Thus, 522 nm (VIS) and 1043 nm (IR) wavelength laser pulses with 1000 kHz PRF could be applied on CIGS TFSC. Figure 4-3 shows an overview of 6 scribing lines fabricated by Yb-doped fiber based fs laser pulses.

![Figure 4-3. Laser scribing on CIGS TFSC by Yb-doped femtosecond laser ($\lambda = 1043$ and 522 nm, $\tau = 400$ fs, PRF = 1 MHz). NA 0.55 objective lens (Mitutoyo M plan Apo, 50X) was used for tight focusing of laser pulses. Various scribing speeds (0.01, 0.02, and 0.05 mm/s) were tested to elucidate an effect of pulse accumulation on CIGS TFSC.](image)

The results indicate that the width of isolation lines was reduced at lower pulse accumulation. (figure 4-4) This trend can be explained by the accumulation of thermal energy on CIGS. As aforementioned in chapter 2, photochemical (or electric) mechanism dominantly occurs in fs laser ablation. However, we could not completely eliminate the thermal effect since the partial energy of excited electrons can be transferred to phonon energy. Thus the temperature of focal zone can be increased and it may return to the initial temperature up to few microseconds later. If laser pulses are irradiated on heated material, more energy can be transferred to material since the optical properties of
material depend on temperature. In our case, pulse-to-pulse time interval was 1 µs that might be shorter than cooling time of material in the processing regime.

The results also indicate that the isolation lines fabricated by both wavelengths (VIS and IR) had similar morphologies. This result can be explained by the beam size at the focus and the optical properties of CIGS. The beam size at the focus of an IR pulse is approximately twice as that of a VIS pulse since the wavelength and the beam size at the focus are proportional. Therefore, larger area was affected by IR pulse than VIS pulse. Furthermore, the beam size affected pulse accumulation since the large beam creates more overlapping area than a smaller beam at the same scanning speed. Thus, more energy can be accumulated by same numbers of IR pulses than VIS pulses. On the other hand, the energy fluence of VIS pulse is approximately four times greater than that of IR pulse since the energy fluence at the focus is inversely proportional to the square of the beam waist. Additionally, the absorption coefficient of CIGS for VIS pulse (~10^5 cm⁻¹) is one order higher than that of IR pulse (~10^4 cm⁻¹). In both cases, single photon absorption is likely since IR (~1.15 eV) and VIS (~2.30 eV) pulses have higher photon energies than the bandgap of CIGS (~1.2 eV). Therefore, more energy was transferred by VIS pulse to CIGS than by IR pulse. As a result, similar isolated lines were fabricated due to compensation of various phenomena that include beam size, pulse accumulation, energy fluence, and absorption coefficient.

Based on our investigation, we could fabricate 550 nm-wide lines on CIGS TFSC by Yb-doped fiber based fs laser. (figure 4-4. (f)) However, the depth of line was insufficient to isolate CIGS layer that was confirmed by electrical measurement. To complete isolation, more energy fluence should be irradiated on the CIGS TFSC. Therefore, various alternatives were considered, which include utilization of amplified fs laser, changing of PRF, adoption of high NA lens, and applying more pulse accumulation via overlapping method.

![Image](image-url)

Figure 4-4. An effect of wavelength and pulse accumulation for fs laser scribing on CIGS TFSC; λ = 1043 nm (a), (b), (c) and λ = 522 nm (d), (e), (f) at 0.01 mm/s (a), (d), 0.02 mm/s (b), (e), and 0.05 mm/s (c), (f). The pulse duration and PRF of processing laser is ~400 fs and 1 MHz, respectively. NA 0.55 objective lens was applied for tightly focusing of processing laser.
4.3.2 Amplified Ti:sapphire femtosecond laser scribing on CIGS thin film solar cell

To apply higher laser pulse energies on CIGS TFSC, amplified Ti:sapphire fs laser ($\lambda = 800$ nm, $\tau \approx 100$ fs, PRF = 1 kHz, and $E_{\text{max}} = 200$ µJ) was employed. Figure 4-5 shows morphologies of isolation lines on CIGS TFSC fabricated by laser pulse energies of 10 and 20 µJ focused via lower NA objective lens (Mitutoyo M Plan Apo, 20X, NA0.28) with scribing speeds of 0.1 and 0.05 mm/s that are respectively equivalent to accumulation of ~60 and ~120 pulses. The result indicates that the effect of pulse accumulation can be negligible for the above speeds. Not only the number of pulses was fewer, but also pulse-to-pulse time interval is long enough (1 ms) for recovering the temperature of CIGS to the initial state. However, the effect of solely the irradiated pulse energy was observed, wherein a wider scribed line was fabricated by higher laser pulse energy. (Figure 4-5)

![Figure 4-5](image)

**Figure 4-5.** An effect of pulse energy and pulse accumulation; scribing line was fabricated by 10 µJ (a), (b) and 20 µJ (c), (d) pulse energies with scribing speeds of 0.1 mm/s (a), (c) and 0.05 mm/s (b), (d). Pulse duration, PRF, and wavelength of processing laser are ~100 fs, 1 kHz, and 800 nm, respectively. Objective lens with NA 0.28 was applied for laser scribing.

Even though the wavelength of laser pulses barely affected the CIGS laser scribing process, laser pulses with shorter wavelength can fabricate narrower lines. Thus, 400 nm wavelength (NUV) pulses were generated via SHG. For laser scribing with NUV pulses, the effects of pulse energy and pulse accumulation were examined. To elucidate the
effect of pulse energy, 8 different pulse energies (10, 20, 30, 40, 50, 60, 80, and 100 µJ) were applied and to investigate the effect of pulse accumulation, 4 different PRFs (20, 50, 100, and 200 Hz) were applied on CIGS TFSC. In this series of experiments, scribing speed (0.2 mm/s) was fixed and pulse accumulation was manipulated by changing the PRF (20, 50, 100, and 200 Hz are equivalent to irradiation by single pulses with a gap, single pulses without a gap, 2 pulses and 4 pulses, respectively). In addition, changing PRF causes change of pulse-to-pulse time intervals, which are 50 ms (20 Hz), 20 ms (50 Hz), 10 ms (100 Hz), and 5 ms (200 Hz).

Optical microscope images of CIGS scribes fabricated by NUV laser pulses with 10-40 µJ indicated that these did not penetrate fully through the molybdenum layer, even at the highest repetition rate of 200 Hz. Thus, laser pulses with higher energies (50, and 60 µJ) were irradiated on CIGS TFSC. (figure 4-6) The results indicate that higher PRF (200 Hz, 4 pulses) could fabricate more fine lines than lower PRF (100 Hz, 2 pulses) in this energy regime. Further increase of pulse energy (80 and 100 µJ) caused delamination of the CIGS film. (figure 4-7)

Figure 4-6. SEM images of CIGS scribes fabricated by 400 nm wavelength laser pulses with various pulse energies: 100 µJ (a), 80 µJ (b), 60 µJ (c), and 50 µJ (d). Scribing speed (0.2 mm/s) was fixed and PRF was changed in order to elucidate the effect of pulse accumulation; 20, 50, 100, and 200 Hz are equivalent to single pulse with gap, single pulse without gap, 2 pulses, and 4 pulses, respectively. The processing laser pulses were focused via NA 0.28 objective lens (Mitutoyo M Plan Apo, 10X).
Since ink-based CIGS film makes relatively poor adhesion between molecules than CIGS films prepared by other methods (evaporation and sputtering), delamination of ink-based CIGS film is possible during the scribing process. In fs laser scribing, the delamination of ink-based CIGS film might be initiated by coulomb explosion and residual stress. It is obvious that higher energy fluence enhances coulomb explosion. Therefore, to prevent the delamination of CIGS film, the pulse energy fluence should be less than the critical value. In our case, critical pulse energy fluences initiating delamination are \( \sim 5.0 \times 10^2 \) J/cm\(^2\) at 200 Hz and \( \sim 4.5 \times 10^2 \) J/cm\(^2\) at 100 Hz. An evidence of localized delamination was visible in the focused ion beam (FIB) cross section of the CIGS scribe fabricated at critical pulse energy fluence. (figure 4-8) The FIB cross-section of CIGS scribes without delamination is shown in figure 4-9 as a comparison.

Based on our investigation of laser scribing on CIGS TFSC with NUV pulses, effective processing conditions were identified, in the range of 50-60 \( \mu \)J pulse energy with PRF of 100 Hz and 200 Hz at the scribing speed of 0.2 mm/s. (figure 4-9, 4-10) With effective processing conditions, we could fabricate isolation lines with \(~8 \mu m\) width on CIGS TFSC.

Figure 4-7. Delamination of CIGS film occurred at laser scribing with 80 and 100 \( \mu \)J pulses.
Figure 4-8. Local delamination of CIGS scribes; fabricated by laser pulses ($\lambda = 400$ nm, $E = 60 \mu$J, and 100 Hz); cross-sectional was exposed by focused ion beam (a) and top view image was taken by SEM (b).

Figure 4-9. CIGS scribes were successfully fabricated by laser pulses ($\lambda = 400$ nm, $E = 60 \mu$J, and 200 Hz); cross-sectional was exposed by focused ion beam (a) and top view image was taken by SEM (b).

Figure 4-10. CIGS scribes were successfully fabricated by laser pulses ($\lambda = 400$ nm and $E = 50 \mu$J) with PRF of 100 Hz (a) and 200 Hz (b).
4.3.3 The effect of overlapping

Finally, the effect of overlapping of processing laser pulses along the isolation lines was examined. (i.e. laser scribing was performed multiple times along the same isolation line.) In this series of experiments, the effect of overlapping was elucidated by two different comparison studies: i) comparison between overlapping and pulse accumulation and ii) comparison between fewer overlaps with high energy and more overlaps with low energy.

For case i) study, Yb-doped fiber based fs laser pulses ($\lambda = 522$ nm, $\tau = \sim 400$ fs, PRF = 100 kHz, and $E = 230$ nJ) were irradiated on CIGS film. (figure 4-11) Results indicate that increasing pulse accumulation could not completely fabricate scribing lines. (figure 4-11 (a)) However, 5 times overlapping of processing laser pulses with speed of 0.01 mm/s could completely fabricate fine isolation lines with $\sim 1$ μm width. (figure 4-11 (b)) The difference between overlapping and pulse accumulation may be based on surface roughness and the amount of absorbed energy. Once the CIGS film surface is modified by fs laser pulses, the absorption characteristics of the sample are altered (in most case, absorbance is increased). In case of overlapping, laser pulses were irradiated on the pre-existing isolation line and the roughness of pre-existing isolation line enhances energy absorption. As a result, we can completely fabricate fine isolation lines with overlapping of low energy laser pulses.

Figure 4-11. Yb-doped fiber based femtosecond laser ($\lambda = 522$ nm, $\tau = \sim 400$ fs, PRF = 100 kHz, $E = 230$ nJ) scribing with NA0.8 objective lens (Nikon, 100X). Various scribing speeds (a) and overlapping times (b) were examined; for overlapping, scribing speed (0.01 mm/s) was fixed.
For case ii) study, Ti:sapphire fs laser pulses (λ = 400 nm, τ = ~100 fs, PRF = 50, 100, and 200 Hz) were irradiated on CIGS film. For a fair comparison, the total amount of energy irradiated on CIGS film was matched, which was single scribing with 15 µJ pulses and 5 times overlapping with 3 µJ pulses. Results indicate that the shape of scribing lines fabricated by overlapping method was better than the other. (figure 4-12) Previous experiment set already shows the fact that laser scribing with higher energy pulses fabricated wider lines. Additionally, fine and deeper lines could be fabricated since second round of laser pulses were irradiated on modified surface. Therefore we can conclude that overlapping of processing pulses with low energy is more proper to fabricate fine scribing lines on the CIGS film.

Figure 4-12. Ti:sapphire femtosecond laser (λ = 400 nm, τ = ~100 fs) scribing with NA0.28 objective lens (Mitutoyo M Plan Apo, 10X). To elucidate the effect of overlapping, total energy irradiated on CIGS film was matched. (1 time overlapping with 15 µJ pulses (a), (c), (e) and 5 times overlapping with 3 µJ pulses)
4.4 Conclusion

The CIGS thin film solar cell was prepared by ink-jet printing method. To fabricate electric isolation lines for monolithic interconnected PV device, Yb-doped fiber based and Ti:sapphire femtosecond laser was applied. First series of experiments indicates that the effect of wavelength can be negligible while the effect of pulse accumulation should be considered in laser scribing by Yb-doped fiber based fs laser. Lines of 550 nm width were fabricated, but did not completely isolate the CIGS film. Thus, an amplified Ti:sapphire fs laser was utilized to apply more energy. In this series of experiments, the effect of pulse accumulation could be negligible, while the effect of pulse energy was significantly occurred. However, delamination occurred at pulse energy of 80 µJ and thereafter. Effective conditions for laser scribing of CIGS film were identified (E = 50-60 µJ, PRF = 100-200 Hz, and λ = 400 nm) and ~8 µm scribing lines were fabricated. Finally, the effect of pulse overlapping was elucidated. The results indicated that overlapping is more effective than other parameters. Therefore, fine isolation lines with ~1 µm could be fabricated by the overlapping method. We can conclude that overlapping of low energy pulses can be a strong candidate for fabricating isolation lines on CIGS film.
Part 2

Transparent materials

Chapter 5

Femtosecond laser ablation of LiNbO₃

5.1 Introduction

Ever since Lithium niobate (LiNbO₃, LN) was discovered as a ferroelectric material in 1949 [72], it has been intensely investigated due to its interesting properties that have strong technological relevance. LN has electro-optical, acousto-optical, nonlinear optical, ferroelectric, photo-elastic, and photo-refractive properties [20] and can be applied to optical waveguides [73-79], resonators, modulators [80], 2D photonic crystals [81, 82], 2D phononic crystals [83], polaritonic devices [84], microdiffraction elements [85], and focusing microstructures [86]. For using LN to previously listed applications, controlled micro/nanopatterns should be fabricated.

To fabricate micro/nanopatterns on the LN surface, various efforts have been performed, including standard photolithography followed by dry or wet etching [73, 87], focused ion beam etching (FIB) [81], and laser processing. [74-79, 84, 88-102] However, it is hard to fabricate sub-micro size patterns with standard photolithography technique and it is too slow to fabricate complete patterns with FIB. Therefore, laser processing has been studied. Micrometer size grooves were fabricated by continuous wave (CW) Ar laser [88], UV CW laser [89], changing of UV light etching resistance of LN [90], and mask projection using nanosecond (ns) KrF laser [91, 92]. Picosecond (ps) laser also applied to fabricate micrometer size patterns [93] and waveguide [74].

Femtosecond (fs) laser could fabricate finer patterns than CW, ns, and ps laser. Optical waveguides of width of ~10 µm [75, 76], ~5 µm [77], ~3 µm [78], and ~1.4 µm [79] were fabricated by fs laser with pulse duration of 40-600 fs. Domain reversal patterns were fabricated by fs laser with pulse duration of 80 fs on y-cut LN crystal surface. [94] Dots with diameter of ~15 µm [95], ~6 µm [96], ~5 µm [97], ~3 µm [84], and ~2 µm [98, 99] were fabricated by fs laser with pulse duration of 50-300 fs. The finest dot fabricated by fs laser pulse irradiation was ~80 nm. [100] Additionally, pulse accumulation effect on fs laser ablation was elucidated [101] and ~100 nm size laser-induced periodic surface structures (LIPPS) in a ~800 nm ablation crater were generated by irradiating 17-pulses of fs laser. [102]

In this study, we study the effects of angle between reference axes (x-, y- and z-axis) of LN crystal (x-cut and z-cut) and laser polarizations (linear and circular polarizations).
We could fabricate the finest dot with \( \sim 45 \text{ nm} \) diameter on z-cut LN crystal surface and less than 100 nm size LIPSS on both x- and z-cut surfaces.

### 5.2 Experimental set up

Figure 5-1 depicts a schematic of experimental set-up. Ti:sapphire fs laser (\( \lambda = 800 \text{ nm} \), \( \tau = \sim 100 \text{ fs} \), and PRF = 1 kHz) was applied to fabricate nanometer size dots on x-cut and z-cut LN crystal wafer (Del Mar Photonics). To fabricate fine nanostructures, frequency doubling (\( \lambda = 400 \text{ nm} \)) was achieved by \( \beta \)-barium borate (BBO) nonlinear crystal and laser beam was focused via high NA objective lens (Nikon, NA=0.8). Laser pulse energy was manipulated by combining a half-wave plate and a polarizing beam splitter (PBS). For pulse accumulation, mechanical shutter (Thorlabs, SH05) and shutter controller (Thorlabs, SC10) were used. To fabricate LIPSS, at least few tens of pulses should be irradiated on a site. Therefore, the shutter was opened for 50 ms to irradiate 50 pulses at same site on LN wafer surface. For analyzing the morphology of ablated craters, both scanning electron microscope (SEM) and atomic force microscopy (AFM) were used.

The primary flats of each wafer (x-cut and z-cut) are perpendicular to z-axis that is parallel to c-axis and the x-axis that is perpendicular to the mirror plane. We determined the reference axis based on hexagonal unit cell and the primary flat of each wafer.

![Figure 5-1. A schematic diagram of the femtosecond laser ablation](image)

*Note: 31.84% of measured energy were irradiated on the sample*
5.3 Result and discussion

5.3.1 Ablation thresholds of LiNbO$_3$ according to crystal orientation

LN belongs to trigonal crystal system and has three-fold rotational symmetry about its c axis. Additionally, it has mirror symmetry about three planes that are 60° apart. In trigonal crystal system, both hexagonal and rhombohedral unit cells can be chosen as a unit cell. In an hexagonal unit cell, the z-axis is parallel to c axis, the y-axis is parallel to one of mirror planes, and the x-axis is orthogonal to the y-z plane. In this study, we chose hexagonal unit cell and both z- and x-cut LN wafers were fabricated by femtosecond laser pulses. The z-cut and x-cut correspond to the z-axis and x-axis being normal to the

Figure 5-2. Ablation of LN according to crystal orientations. Frequency doubled Ti:sapphire femtosecond laser pulses ($\lambda = 400$ nm, $\tau = \sim 100$ fs, PRF = 1 kHz) were irradiated on LN surface. Both linear polarized pulses and circular polarized pulses were tested. For fabricating craters, 50 pulses were accumulated.
wafer surfaces, respectively. Meanwhile, laser light is polarized and the angle of irradiating laser pulses with respect to the reference axes in the crystal could affect the ablation of LN. Therefore, linearly polarized laser pulses were irradiated parallel to each reference axis (x-, y-, and z-axis) of LN and circularly polarized laser pulses were irradiated on two different LN crystal wafers (z- and x-cut) surfaces. Figure 5-2 shows an overview of the machined ablation craters. The result indicates that ablation of LN by both linearly and circularly polarized laser pulses were affected by crystal orientation.

![Graphs showing the relationship between square of ablated crater diameter and laser pulse energy.](image)

Figure 5-3. The square of ablated crater diameter ($D^2$, $\mu m^2$) versus laser pulse energy (F, J/cm$^2$). Note that x-axis of plots (F) is log scale.

The ablation thresholds of each case were determined from the relation between the square of ablated crater diameter and the logarithm of the pulse energy fluence: [31]
where $D$ is the diameter of ablated crater, $\omega_0$ is beam waist ($1/e^2$ radius), $F$ is laser pulse fluence ($J/cm^2$), and $F_{th}$ is the ablation threshold of material. For a statistical approach, 10 craters per each case were fabricated. Figure 5-3 depicts the relation between ablated area and laser pulse energy fluence. Results indicate that real beam waist ($\omega_0$) was in the range of 465-490 nm. Laser pulses with linear polarization parallel to x-axis (perpendicular to c-axis and the mirror planes) induce lowest ablation threshold (0.40 $J/cm^2$), to y-axis (parallel to mirror planes) the highest ablation threshold (0.90 $J/cm^2$), and to z-axis (parallel to c-axis) a moderate ablation threshold (0.60 $J/cm^2$). For the case of circularly polarized laser pulses on the LN crystal, both laser pulses irradiated on x-cut (0.25 $J/cm^2$) and z-cut (0.38 $J/cm^2$) surface were lower than irradiating linearly polarized laser pulses on the LN. Compared with previous research (0.52 ± 0.06 $J/cm^2$ for 80 pulses) [101], we revealed more detailed ablation threshold by changing the angle of the irradiating laser pulses with respect to the crystal orientation.

5.3.2 Laser induced periodic structures on LN crystal surface

Ever since laser-induced periodic structures were observed on a semiconducting material surface that exposed to Ruby laser pulses,[14] many researchers have attempted to generate LIPSS on various materials (metal, semiconductor, dielectric, and etc.). The LIPSS can be categorized as low-spatial-frequency LIPSS (LSFL) and high-spatial-frequency LIPSS (HSFL).[15] The LSFL is generated by interference between irradiating laser pulses and surface electromagnetic wave (SEW) at the surface. [16, 103-106] The period ($\Lambda$) of LSFL scales with the wavelength ($\lambda$) of irradiating laser pulses or $\lambda/n$. (n is refractive index of material, $n < 2$) [17, 107-109] In most cases, LSFL is perpendicularly generated to polarization of irradiating laser pulses. The HSFL is generated in transparent materials and the $\Lambda$ of HSFL is smaller than $\lambda/2$. The HSFL could be generated both perpendicular [17, 109] and parallel [110, 111] to polarization of irradiating laser pulses. The origin of HSFL generation is controversial, but three possibilities can be considered, which are the effect of second harmonic generation (SHG), [17] interference between irradiating laser pulses and surface wave (polariton) [18], and self-organization. [19]

Yu et al. reported a fabricating LIPSS ($\Lambda$ = ~100 nm) on z-cut LN crystal surface by accumulation of 17-pulses of fs laser ($\lambda$ = 800 nm, $\tau$ = 50 fs, PRF = 1 kHz).[102] However, the effect of the angle between linearly polarized laser pulses and LN crystal orientation on formation of LIPSS has not been elucidated. In this study, LIPSS was fabricated on four different cases by irradiating linearly polarized laser pulses parallel to x-, y-axes on z-cut and z-, y-axes on x-cut LN wafer surfaces. The results indicate that similar widths (78 ± 12 nm) of LIPSS were generated for each case, with the sole exception corresponding to irradiation of linearly polarized laser pulses parallel to z-cut, y-axis (92 ± 12 nm). (figure 6-4) The fabricated LIPSS belongs to the HSFL regime since $\Lambda$ is smaller than $\lambda/2$. As aforementioned, three possibilities can be considered regarding the origin of LIPSS on the LN crystal surface. Even though the width was similar, all cases had slightly different morphologies. That may indicate that the crystal orientation
affects the generation of LIPSS on LN surface. The effect of crystal orientation could support the possibility of SHG, interference, and self-organization. The SHG occurs via high density of electrons and it is possible that certain orientation absorbs more energy than other orientations. The interference can also be affected by crystal orientation since the propagation of polaritons can be affected by the characteristics of atomic bonds. In addition, self-organization can be affected by crystal orientation as well. For further understanding of the physical origin of the observed structures, we should perform additional experiments, including time resolved study of electron distribution, time resolved spectroscopy, etc.

![Figure 5-4](image)

**Figure 5-4.** Laser induced periodic structure on LN surface fabricated by Ti:sapphire femtosecond laser pulses ($\lambda = 400$ nm, $\tau = \sim 100$ fs, PRF = 1 kHz, shutter open = 50 ms, $F = 1.57$ J/cm$^2$). Processing laser pulses were focused via objective lens (Nikon, 100X, NA 0.8). For elucidating the effect of an angle between laser polarization and crystal orientation, linearly polarized laser pulses parallel to (a) z-cut, x-axis, (b) z-cut, y-axis, (c) x-cut, z-axis, and (d) x-cut, y-axis were irradiated. The arrow indicates a polarization direction of laser pulses.

### 5.3.3 Fabrication a dot with $\sim 45$ nm diameters on LN crystal surface

The smallest dot ever fabricated on the LN surface (z-cut) was $\sim 80$ nm. [100] In this study, we could fabricate dots with diameter of $\sim 45$ nm on z-cut surface by irradiating 50-pulses parallel to x-axis. The fabrication of $\sim 45$ nm size dot was confirmed by both SEM and AFM analysis. (figure 6-5)
5.4 Conclusion

Fine nanostructures on LN are desired because of relevance for significant technical applications. In this study, we performed the fabrication of nanostructures on LN wafer surfaces by irradiating femtosecond laser pulses. Through experiments, we revealed that the ablation threshold was affected by the angle between the polarization direction of the laser pulses and the crystal orientation. The highest ablation threshold was 0.90 J/cm$^2$ (irradiation of linearly polarized laser pulses parallel to y-axis) and the lowest ablation threshold was 0.25 J/cm$^2$ (irradiation of circularly polarized laser pulses on x-cut wafer surface). Additionally, the generation of LIPSS on LN surface was affected by the angle between the polarization direction of the laser pulses and the crystal orientation. The period for the orientations examined was (78 ± 12 nm), with the exception when linearly polarized laser pulses were irradiated parallel to z-cut, y-axis (92 ± 12 nm). Finally, we could fabricate ~45 nm size dots on z-cut wafer by irradiating linearly polarized laser pulses parallel to x-axis.
Chapter 6

Helical channel with circular cross section fabricated by femtosecond laser

6.1 Introduction

Lab-on-a-chip (LOC) devices for chemical, biological, and medical applications have been studied intensively in the last few decades. The LOC devices are based on microfluidic functions such as mixing, separating, and transporting. The mixing in LOC is dominated by diffusion because of the low Reynolds number ($Re$) due to small hydraulic diameter as the typical channel diameter of LOC device is ~100 µm. Because the diffusion time for complete mixing of proteins in the 2D channels can reach up to few tens of seconds, the mixing channel length is a main contributor to the enlargement of the total size of LOC devices.

Mixing channels can be generally categorized as “active micromixers” and “passive micromixers”.[21-23] In contrast to active micromixers that require additional external energy input, passive micromixers only need energy for driving the flow. Despite this advantage, passive micromixers need longer mixing channels than active micromixers, since active micromixers enhance the mixing by generating transverse flow and augment the contact area between the mixing agents. In terms of energy consumption, there has been interest in passive micromixers and hence researches that are focused on reducing of mixing channel length by generating transverse flow without additional external energy input.

For generating a transverse flow in passive micromixers, microfluidic channels with ridges on its floor was proposed by Stroock et al.[24] Transverse flow in the microchannels can significantly increase the mixing efficiency and reduce the length of channel. In order to generate transverse flows for enhancing the mixing more effectively, various types of three-dimensional (3D) passive micromixers have been proposed in the last decade.[112-124]

Helical channel with circular cross section is one of the most promising geometries for generating transverse flows. In these channels, secondary circulating flows are generated as revealed by Dean in the toroidal pipe (helical pipe with zero pitch)[125, 126] and subsequently have investigated by numerous groups.[25, 127-139] Even though there had been an argument about which factor contributes more to generate the secondary circulating flows in the helical pipe,[128, 130, 131] it was verified that the torsion and curvature of the pipe determine the pattern of secondary circulating flows.[25, 132-134] Furthermore, Liu and Masliyah revealed the critical condition that determines the number of vortices across the cross sectional plane.[25] When the Liu-Masliyah number (LM, $\gamma$ and $\gamma^*$) is smaller than 0.039 (for $Dn < 20$) or 0.2 (for $Dn \geq 20$), two vortices are formed. In contrast, a single vortex is formed when LM is bigger than these critical values. Two vortices with opposing rotations can enhance the mixing rate in the microchannel.
In this study, 3D helical passive micromixer with circular cross section is demonstrated. Several mixing conditions were tested to optimize the micromixer. The helical microchannel was fabricated inside fused silica with femtosecond laser irradiation and chemical etching (FLICE) technique.[26] The FLICE technique consists of two steps: (1) the direct writing of waveguides in the fused silica with femtosecond laser by multiphoton absorption (MPA) and (2) the chemical etching of the waveguide. It should be noted that only the waveguide is etched due to the different etching rate between modified and unmodified regions of fused silica. The optical band gap of fused silica is ~8 eV[27] and the laser wavelength used in this work is 522 nm (2.38 eV). Thus, the waveguide inside fused silica is generated by multi-photon absorption (MPA).[140] To enhance MPA, high density of photons should be irradiated onto the target material. Thus, femtosecond laser is the most effective optical energy source for internal writing in fused silica. Furthermore, localized MPA occurs within the focal zone without inflicting damage elsewhere. Therefore, the femtosecond laser direct writing technique is an excellent tool for fabricating three-dimensional structures in semi-transparent materials.

The Rhodamine B (DR = 3.6×10^{-10} m^2/s)[141] and Streptavidin-Alexa conjugate (DS = 5.8×10^{-11} m^2/s)[142] were used as mixing materials. The Rhodamine B (RB) is one of the most common fluorescent dyes for visualizing liquid flow in the microchannel. The Streptavidin is extensively used in biology/bioengineering research and in order to tracking the diffusional motion of Streptavidin molecules, the Streptavidin-Alexa (SA) conjugate (Alexa Flour® 488 Streptavidin, Invitrogen) was used. Because of its size (diameter of 7.6 nm), the SA conjugate has relatively low diffusivity. Thus, it is proper material for testing the mixing efficiency of our channel.

Considering the development of a concentration boundary layer, the straight microchannel length should reach up to few hundreds of centimeters to achieve complete mixing of SA conjugate with DI water. In this study, both simulations and experimental results showed that the transverse flow patterns and the flow residence time in the helical channel affect mixing efficiency. With optimized flow conditions, we can significantly reduce the length of the mixing channel from few hundreds of centimeters to a few hundreds of micrometers.

6.2 Experimental

Figure 6-1. shows a schematic of the experimental set up for direct writing of waveguide inside fused silica by femtosecond laser irradiation. A Yb-doped fiber based femtosecond laser (pulse duration (τ) = ~400 fs, pulse repetition frequency (PRF) = 500 kHz, FCPA μJewel D-400, IMRA America, Inc.) is used for waveguide writing. Waveguide-writing by Yb-doped fiber based femtosecond laser has been performed by multiple groups.[143, 144] Previous research has shown that frequency doubled laser pulses of λ = 522 nm wavelength write better quality waveguides inside bulk fused silica than pulses of the fundamental wavelength (λ = 1045 nm).[143, 144] Therefore, a Lithium triborate (LBO) second harmonic nonlinear crystal (Newlight Photonics) was utilized for frequency doubling whose efficiency was enhanced by a collection lens.

The etching rate of the fabricated waveguide was affected by the orientation of laser pulse polarization with respect to the waveguide-writing direction. (figure 6-2) To
fabricate a channel with constant cross-section, the polarization effect should be diminished. Accordingly, a quarter wave plate was inserted in the beam path to generate circular polarization.

![Figure 6-1. Schematic of experimental set up for femtosecond laser waveguide writing; Dotted line indicates that optical path is vertical.](image)

Our previous work tested various pulse energies and scanning speeds in order to find optimal processing regimes for our fabrication set-up.[145] The sole exception in the present work was that we used PRF of 500 kHz rather than 1 MHz.[145] This variation is minor consequence, as the laser pulse fluence is the main factor affecting the quality of waveguide writing.[144] Thus, ~180 nJ/pulse on the fused silica was used for waveguide writing; the maximum energy of frequency doubled laser pulse was 400 nJ and the efficiency of our optical set up was ~ 45%. The laser pulse energy level was manipulated by a combination of half wave plates and a polarizing beam splitter (PBS). Since
aberration plays a role for numerical aperture (NA) over 0.6 and self-focusing appears for NA less than 0.4, we used a lens of 0.55 NA (Mitutoyo M Plan Apo, 50X) to avoid these effects.[146]

![Top view](image)

**Top view**

Figure 6-2. Polarization effect on chemical etching; (a) Top view image of 12.5% HF etching. The arrow indicates a polarization direction of laser pulses. Energy fluence: 6.4 J/cm², scan speed: 100 µm/s, and NA of objective lens: 0.55 are applied on this experiment. (b) Side view schematic of chemical etching experiment.

For writing 3D helical waveguides in bulk fused silica, a 3-axis mechanical bearing direct-drive linear stage (Aerotech, ANT95-50-L-Z-RH on the ANT95-XY-MP) was used. The scanning speed was set at 100 µm/s, based on previous work.[145] The waveguide in the bulk fused silica was etched by diluted hydrofluoric acid (HF): 49% HF (10 ml) to DI water (30 ml). This chemical reaction can be expressed as: $6\text{HF} + \text{SiO}_2 = \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$. The hexafluorosilicic acid and water can reduce the etching rate. Therefore, we should enhance liquid circulation in the channel in order to maintain stable etching rate. The waveguide embedded fused silica was therefore placed in a sonic bath with diluted HF solution for 200 minutes. The total length of channel (including the inlets, the outlet and the helix) was ~1500 µm.

After carrying out the waveguide writing and etching process, a polydimethylsiloxane (PDMS) cover with inlets and outlet holes was bonded on top of the fabricated sample by corona bonding process.[147] Syringes ran by syringe pumps were connected to the inlets. One syringe was filled with DI water and the other with fluorescent dyes: RB (Sigma, $\lambda_{ex} = 533$ nm, $\lambda_{em} = 627$ nm) and SA conjugate (Invitrogen, $\lambda_{ex} = 495$ nm, $\lambda_{em} = 519$ nm). Initial concentrations of RB and SA conjugate were $C_R = 2.26 \times 10^{1}$ mol/m³ and $C_S = $
3.66×10^{-3} \text{ mol/m}^3, respectively. Flow rates used in this study were from 0.2 ml/h to 2.0 ml/h that result in Re range from 2.82 to 28.2 for helical microchannels with hydraulic diameter of 50 µm.

The fabricated helical micromixer was placed on an inverted microscope (Olympus, IX71) equipped with a mercury lamp and filter cubes for acquiring images of fluorescent dye through the channel by a digital CCD camera (Retiga 2000R cooled, Qimaging). The images were taken a few minutes after setting the flow rate. To prevent saturation of fluorescence images, the illumination power was controlled by a diaphragm.

6.3 Result and discussion

6.3.1 Fabrication result

![Fabrication result images](image)

Figure 6-3. Fabrication results of (a) helical micromixer and (b) linear micromixer with circular cross section. (c) Parameters of helix; K is torsion of helix, R is radius of helix, and r is radius of cross section.
The helical microchannel with circular cross section fabricated by the FLICE technique is shown in figure 6-3 (a). A straight channel with circular cross section was also fabricated for the purpose of running comparative control of mixing experiments (figure 6-3(b)). The length of the straight channel was matched with the helical channel flow path length for verifying the effect of the helical configuration. Figure 6-3(c) depicts the helix parameters; $2\pi K$ is the helix pitch, $R$ is the helix radius, and $r$ is the radius of the circular cross section. The circular cross section diameter is $50 - 55 \mu m$, the helix curvature, $\kappa$, is $1.65 \times 10^2 \mu m^{-1}$, and the helix torsion, $\tau_h$, is $7.58 \times 10^{-3} \mu m^{-1}$, respectively. The helix curvature and torsion can be calculated using the following equations:

$$\kappa = \frac{R}{R^2 + K^2}, \tau_h = \frac{K}{R^2 + K^2}$$

To calculate the Dean number ($Dn = Re \delta^{1/2}$), the Germano number ($Gn = Re \eta$), and the Liu-Masilyah number ($\gamma = \eta/(\delta Dn)^{1/2}$ for $Dn > 20$ and $\gamma^* = \eta/(\delta Re)$ for $Dn < 20$), a normalized curvature ($\delta = kr$) and a normalized torsion ($\eta = \pi r$) were adopted.

6.3.2 Mixing percentages

We quantified the mixing efficiency using the mixing percentage from Johnson et al.[148] The mixing percentage is expressed according to the following equation:

$$Mixing\ percentage = \left(1 - \frac{\frac{1}{N_t} \sum_{i=1}^{N_t} (I_i - I_{i,\text{Perf.mix}}^0)^2}{\frac{1}{N_t} \sum_{i=1}^{N_t} (I_i^0 - I_{i,\text{Perf.mix}}^0)^2}\right) \times 100$$

where $N_t$ is the total number of pixels, $I$ indicates the normalized intensity with respect to maximum intensity of each data set, the subscript $i$ indicates the $i^{th}$ pixel, the superscript Perf.mix indicates the case that the entire channel is filled with fluorescent dye, and superscript 0 indicates the case where no diffusion has occurred. Intensity values corresponding to perfect mixing where fluorescent dyes were infused into both inlets ($I_{i,\text{Perf.mix}}$) were acquired. Intensity values for the zero diffusion ($I_i^0$) case were calculated from perfect mixing data. To calculate $I_i^0$, $I_{i,\text{Perf.mix}}$ were doubled from the channel edge to the middle point and diminished from the middle point to the other edge. (figure 6-4) The middle point is determined by matching integration values of perfect mixing and zero diffusion intensities; the integrated intensity in the perfect mixing case is equal to the integrated intensity in the zero diffusion case. Intensity distributions along the radial distance are depicted on figure 6-4 as well as $I_{\text{Perf.mix}}$ and $I_0$. At low $Re$ case, the intensity distribution approaches the perfect mixing case, but at higher $Re$ cases, it approaches toward zero diffusion assumption.
6.3.3 Characteristic length and entrance length of concentration boundary layer

In the low Re regime, the flow is laminar and the mixing is dominated by diffusion. This could be quantified by characteristic length or entry length of the concentration boundary layer. The characteristic length can be calculated from following equation:

\[ x_c = u_m t = \frac{Q}{\pi D_{diff}} \]

where \( x_c \) is the characteristic length, \( u_m \) is the mean velocity of flow in channel, \( t \) is the diffusion time, \( Q \) is the flow rate, and \( D_{diff} \) is the diffusion coefficient of the fluorescing agent. The diffusion coefficient of RB (\( D_R = 3.6 \times 10^{-10} \) m\(^2\)/s in 21.5 °C water) was taken from previous work\[141\] and that of the SA conjugate (\( D_S = 5.8 \times 10^{-11} \) m\(^2\)/s) was estimated by the Stokes-Einstein equation.\[142\] The Stokes-Einstein equation is given below:

\[ D_S = \frac{kT}{6\pi \eta_{water} R_{str}}. \]

where \( k \) is the Boltzmann constant, \( \eta_{water} \) is the water viscosity, and \( R_{str} \) a radius of Streptavidin (3.1 nm). For the SA conjugate, the estimated diffusion coefficient \( D_S \) is calculated to be 5.8 \times 10^{-11} \text{m}^2/\text{s} since the size of Alexa fluorescent nanoparticle is 1.4 nm and the diameter of SA conjugate becomes 7.6 nm. Calculated characteristic lengths of RB are 9.82 cm (\( Re = 2.82 \)) ~ 98.24 cm (\( Re = 28.18 \)) and SA conjugate are 60.98 cm (\( Re = 2.82 \)) ~ 609.79 cm (\( Re = 28.18 \)), respectively.
The entry length of a laminar concentration boundary layer in a circular tube can be expressed as follows:

\[
\left( \frac{x}{d} \right) \approx 0.05 \times Re \times Sc = 0.05 \times \frac{\nu_d}{D_{diff}},
\]

where \(x\) is the entry length, \(d\) is diameter of the circular channel, \(Sc\) is the Schmidt number, \(U\) is the mean flow velocity, and \(D_{diff}\) is the diffusion coefficient. The calculated entry length of RB is 1.96 cm \((Re = 2.82)\) ~ 19.65 cm \((Re = 28.18)\) and SA conjugate is 12.20 cm \((Re = 2.82)\) ~ 121.96 cm \((Re = 28.18)\), respectively.

6.3.4 Numerical analysis

To increase the mixing rate in the laminar flow regime, we should enlarge the contact area between the flow components. This can be accomplished by inducing transverse flow in microfluidic channels. The transverse flow can be enhanced by increasing the flow rate. However, at faster flows, the residence time through the microchannel becomes shorter, and the diffusive transport correspondingly weaker. Consequently, there should be an optimal condition for our 3D helical microchannel with fixed geometry \((R, \kappa, \tau, \text{and } r)\) compromising these competing effects.

Prior to performing experiments, a range of Re was determined computationally. The COMSOL Multiphysics software (version 4.3) was used for modeling transport helical microchannels via an embedded solver for the Navier-Stokes equations (laminar flow physics) and the convection-diffusion equation (transport of diluted species physics). For the numerical analysis, the channel cross sectional radius was taken at 25 µm. Ten cases \((2.82 \leq Re \leq 28.2, \Delta Re = 2.82)\) for SA conjugate were analyzed and initial concentration values were matched with experimental conditions \((C_S = 3.66 \times 10^{-3}\text{ mol/m}^3)\).

Figure 6-5 shows the calculated concentration distribution of the fluorescing agent and z-direction (i.e. direction of transverse flow) velocity vectors at selected positions (at the positions of half, one and a half, and two helical turns) for \(Re = 5.64, 16.91, \text{and } 28.18\). For \(Re = 5.64\), a single vortex is formed in the channel \((Dn = 5.12, Gn = 2.14, \text{and } \gamma^* = 0.081 > 0.039)\). The circular secondary flow motion forms a sinusoidal contact boundary between the SA conjugate and the DI water (figures 6-5 (d), (e), (f)). In contrast, double vortices are formed in the channel for \(Re = 16.91\) after experiencing one and half helical turns (figure 6-5 (h), \(Dn = 15.37, Gn = 6.40, \text{and } \gamma^* = 0.027 < 0.039\)), hence completely reversing the course of the two streams and further increasing the mixing rate (figures 6-5 (h), (i)). For the higher \(Re = 28.18\), the cross sectional view shows less effective mixing (figure 6-5 (k), (l)) than the mixing with \(Re = 16.91\) since the flow through the helix is too fast. The mixing percentage for \(Re = 28.18\) is 71.40% and that for \(Re = 16.91\) is 85.36%. (figure 6-6). The calculation indicates that the residence time for \(Re = 28.18\) is 1.5 ms and that for \(Re = 16.91\) is 2.6 ms, and the respective diffusion lengths are 0.3 µm and 0.39 µm. As a result, the most effective mixing was obtained for \(Re = 16.91\) case. In addition, the numerical analysis reveals that a single vortex is formed up to \(Re = 11.27\), while double vortices are developed thereafter. Consistent with the simulations, we therefore set the experimental range from \(Re = 2.81\) to \(Re = 28.18\).
Figure 6-5. COMSOL simulation result of mixing Streptavidin-Alexa flour® 488 conjugate and DI water; laminar flow and transport of diluted species physics are applied for solving a mixing problem. Black arrow indicates z directional velocity and color indicates a concentration of fluorescing agent. Rainbow color contour: red represents higher concentration and blue represents lower concentration. (a), (b), (c) indicates a location of cross sections, (d), (e), (f) for Re = 5.64, (g), (h), (i) for Re = 16.91, and (j), (k), (l) for Re = 28.18 cases, respectively.
6.3.5 Mixing in a straight channel with circular cross section

Mixing of SA conjugate barely occurred within 800 μm in a straight microchannel and the flow rate effect was negligible (figure 6-7 (a)). However, the RB mixing shows a slightly different trend (figure 6-7 (b)). As the Re was increased, the mixing percentage increased as well. This trend could reflect the role of advection in the mixing. In T-typed micromixers, as the Re increases, three different laminar flow regimes occur: stratified flow (for low Re), vortex flow (for moderate Re), and engulfment flow (for high Re).[149] Except in the low Re cases, transverse flow is formed. As a result, the mixing percentage increases with the Re. Though we cannot directly compare our results with previous reports that used T-type micromixers with rectangular cross sections, transverse flow can be formed more easily in a T-type micromixer with circular cross section than rectangular cross section. Thus, vortex flow regime may occur at slightly lower Re in a channel with circular cross section. In the vortex flow regime, as the flow rate increases, transverse flow is enhanced due to enlargement of the contact area between the flow components. Consequently, diffusivity determines the mixing percentage. Since the diffusivity of RB is one order higher than that of the SA conjugate, the mixing rate of RB is correspondingly faster. Hence, the mixing percentage of RB was increased within interested flow rate regime while it was maintained for SA conjugate mixing. (figure 6-7) Even though the mixing percentage cannot exceed 60% (for Re = 28.18) at 800 μm from the confluence of two inlets. (figure 6-7 (b))
6.3.6 Mixing in the helical channel with circular cross section

To analyze the helical geometry effect on mixing, intensity data were acquired in the proximity of the confluence (A in figure 6-8) and downstream of the helix (B in figure 6-8). The shortest direct distance and flow path length from A to B is 400 µm and 800 µm, respectively. Figure 6-8 (a) shows mixing percentages of SA conjugate with DI water according to $Re$ in the helical microchannel. The mixing percentage is in the range of 90% for $Re \leq 14$, and then decreases. Figure 6-8 (b) shows mixing percentages of RB with DI water in the helical microchannel. In this case, the mixing percentage reaches 85% for $Re = 5.64$ and decreases thereafter. As aforementioned, transverse flow would increase mixing while the decreasing trend is attributed to shortened flow residence time in the helical microchannel. For the SA conjugate case, an increasing trend of mixing is not apparent. Since the intensity data were acquired from the top view images rather than
cross sectional images, it is possible that horizontal flow delamination or a horizontal contact boundary was formed at position B in the low Re regime. However, according to simulations (figure 6-5 (f)), the contact boundary is sinusoidal, implying that neither horizontal delamination of flow nor horizontal contact boundaries were formed. Instead, the molecular size of RB (~1.8 nm diameter) and SA conjugate (~7.6 nm diameter) may cause the measured departure. The drag force exerted on the fluorescing nanoparticles by the transverse flow is proportional to cross sectional area of the particles. Therefore, the helical geometry affects the SA conjugate more than the RB, and the mixing percentage of SA conjugate in the low Re regime should be correspondingly higher than that of RB. Indeed, the mixing percentage of SA conjugate at position B was reached around 90% for low Re (≤ 11.27). On the other hand, the mixing percentage of RB at position B reached around 85% for Re = 5.64. The mixing percentages for the same Re are about 2~3 times higher with the helical channel than that with straight channel though the shortest direct distance of channel is half long. (Figure 6-8)

Figure 6-8. Mixing percentage in the helical micromixer: (a) Streptavidin Alexa Fluor® 488 conjugate with DI water and (b) Rhodamine B with DI water. A linear distance between A and B is 400 µm.
6.4 Conclusion

In this study, we fabricated three-dimensional helical microchannels in fused silica using FLICE technique. Mixing of RB and SA conjugate with DI water was observed in these helical microchannels within a short distance (about 400 µm) from the confluence of the streams. Comparison with our analytical estimates of the concentration entry length and the characteristic length that both imply that few hundreds centimeters are needed for complete mixing of proteins, indicates that the helical microchannels significantly reduced the micromixer size.

Numerical analysis was utilized to identify effective conditions for mixing accounting for the compensation between transverse flow patterns and flow residence time in the helical microchannel. Accordingly, the mixing percentage could reach up to 85.36% at $Re = 16.91$ for SA conjugate. Experimental results supported the numerical analysis predictions. Even though the mixing percentage could not exceed 60% in the straight microchannel with circular cross section, it reached 85% ($Re = 5.64$) and 90% ($Re \leq 14$) for RB and SA conjugate in the 3D helical microchannel, respectively.
Chapter 7

Conclusion

Femtosecond laser processing was studied, in the context of high-aspect ratio drilling on thin and brittle PV semiconducting material, laser scribing on ink jet printed CIGS thin film solar cells, laser induced periodic surface structures on lithium niobate wafer, and fabrication of three dimensional helical microchannel in fused silica. In our study, since the materials have wide bandgap, fs laser ablation was dominated by nonlinear mechanisms that include multi-photon ionization, tunneling ionization, and avalanche ionization. The nonlinear mechanism enhanced interesting phenomena such as self-action of light, periodic surface structure, and creation of damage only at the focal zone. We applied two different fs lasers to our samples, which are Ti:sapphire fs laser and Yb-doped fiber based fs laser. For further understanding of each process, various images that include SEM images, emission images, shadowgraphs, FIB cross sectional images, and optical microscopy images were analyzed. In some studies, SHG was required for various reasons, thus LBO and BBO crystal were utilized to achieve frequency doubling of pulses. The energy of fs laser pulses was manipulated via combination of half-wave plate and polarizing beam splitters. The pulse energy was measured via power meter and energy meter. For providing sufficiently high energy fluence, fs laser light was focused via various objective lenses.

In the fs laser drilling on thin c-Si and mc-Si wafer, the self-action of laser light was initiated. As a result, depth of focus was elongated and reduced the total number of shots to fabricate via holes in 160~170 µm thickness Si wafers. Through the cross-sectional analysis, we could reveal the presence of two different regimes, which are drilling via self-guided beam and wall-guided beam. For further decreasing of total shots, the placement of sample was translated. In our regime, the transition of sample toward the objective lens was effective for reducing the total number of shots. In the shadowgraph analysis, we found the merging of two shocks. One was initiated by explosive ablation from the surface and the other was triggered by air breakdown. In the future, additional experiments can help us to understand of the effect of air breakdown in material ablation. In addition, we can fabricate the wrap-through PV devices and evaluate the efficiency of cells.

In the fs laser scribing on ink jet printed CIGS thin film solar cells, the effect of various parameters that include pulse accumulation, wavelength, pulse energy, and overlapping were elucidated. In our processing regime, the effect of wavelength could be diminished due to compensation between beam size, pulse accumulation, energy fluence, and absorption coefficient. On the other hand, for high PRF fs laser processing, pulse accumulation effect cannot be ignored, while it can be negligible in low PRF fs laser processing. The results indicate the presence of the critical value that initiates delamination of CIGS thin film. To avoid delamination and fabricate fine isolation lines, overlapping method was tested. Our results indicate that the overlapping is effective scribing method to fabricate thin films that has a low adhesion layer. In the future, the efficiency loss by isolation lines can be tested. In addition, for precise processing of
CIGS thin film solar cell, in situ laser induced breakdown spectroscopy can be developed.

In fs laser ablation on lithium niobate wafer, we could reveal the effect of crystal orientation of LN and polarization of laser light. The LN belongs to trigonal crystal system and can have two different unit cells, which are hexagonal and rhombohedral unit cells. We chose the hexagonal unit cell and all reference axes were based on that. The results indicate that the ablation threshold was affected by the angle between crystal orientation and polarization of laser light. The highest ablation threshold was 0.90 J/cm² (irradiation of linearly polarized laser pulses parallel to y-axis) and the lowest ablation threshold was 0.25 J/cm² (irradiation of circularly polarized laser pulses on x-cut wafer surface). Additionally, the angle between the polarization direction of the laser pulses and the crystal orientation also affected to periodic surface structures. The period was (78 ± 12 nm) except when linearly polarized laser pulses were irradiated parallel to z-cut, y-axis (92 ± 12 nm). Finally, we could fabricate ~45 nm size dots on z-cut wafer by irradiating linearly polarized laser pulses parallel to x-axis. In the future, we can fabricate the 2D photonic crystal pattern with nanometer size dots. In addition, the time resolved spectroscopy study can help to understand the origin of HSFL.

Finally, three-dimensional helical microchannel was fabricated in fused silica by fs laser irradiation and chemical etching technique. Laser light interacts with transparent dielectric materials via nonlinear mechanisms. Therefore, absorption can occur only in the focal zone without inflicting damage elsewhere. The three dimensional helical waveguide was fabricated by fs laser irradiation and the damaged zone was selectively etched by diluted HF solution. As a result, we could fabricate 3D helical channel (κ = 1.65×10⁻² μm⁻¹, τk = 7.58×10⁻³ μm⁻¹, and d = 50 ~ 55 μm). For understanding fluidic and diffusional transport, numerical analysis was performed. The numerical analysis points to effective mixing conditions due to compensation between the residence time of the flow in the helix and the transverse flow patterns. This result was tested via experiments and we could reach up to ~90% of mixing within 400 μm distance from the confluence. In the future, we may fabricate 3D helical channels with varying curvature and torsion. These channels can be applied to lab-on-a-chip devices, for example in particle separation and purification of water.
References


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