Photophysical And Photochemical Factors Affecting Multi-photon Direct Laser Writing Using The Cross-linkable Epoxide Su-8

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PHOTOPHYSICAL AND PHOTOCHEMICAL FACTORS AFFECTING MULTI-PHOTON DIRECT LASER WRITING USING THE CROSS-LINKABLE EPOXIDE SU-8

by

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ABSTRACT

For the past decade, the epoxy based photoresist SU-8 has been used commercially and in the lab for fabricating micro- and nano-structures. Investigators have studied how processing parameters such as pre- and post-exposure bake temperatures affect the resolution and quality of SU-8 structures patterned using ultraviolet or x-ray lithography. Despite the advances in understanding the phenomena, not all of them have been explored, especially those that are specific to multi-photon direct laser writing (mpDLW). Unlike conventional exposure techniques, mpDLW is an inherently three-dimensional (3D) process that is activated by nonlinear absorption of light.

This dissertation reports how several key processing parameters affect mpDLW using SU-8 including pre-exposure bake duration, focal depth, incident laser power, focal-point scan speed, and excitation wavelength. An examination of solvent content of films at various stages in the mpDLW by $^1$H-NMR shows that even moderate solvent content (over 1 wt-%) affects film viscosity and photoacid diffusion lengths, and can greatly affect the overall fidelity of small features. A study of micro-fabricated feature size versus writing depth in the material shows that even slight refractive index mismatch between SU-8 and the medium between it and the focusing objective introduces spherical aberration that distorts the focus, causing feature size to decrease or even increase in size with writing depth, depending on the average exposure power used. Proper adjustment of the average exposure power was demonstrated as a means to fabricate more uniform features with writing depth. Third, when varying the power and scan speed, it was observed that the feature-size scales with these two parameters in a manner that is consistent with a three-photon absorption mechanism at an excitation wavelength of 800 nm. When an
excitation wavelength of 725 nm is used, the feature-size scaling becomes consistent with that of two photon absorption. This shows that the photoinitiators in the SU-8 can be activated by either two- or three-photon absorption over this wavelength range. Using an irradiance of ~2 TW cm\(^{-2}\) and elongated femtosecond pulses resulted in an observed fourth order power dependence. This observation is in agreement with the literature and suggests that the effective absorptive nonlinearity is also sensitive to pulse duration. These findings will be useful for creating accurate models of the process of mpDLW in SU-8. These models could be used to optimize the processing parameters and develop new processing methods and materials for high-resolution fabrication of robust 3D microstructures. Some of the findings were used to develop a method for fabricating functional microlenses on the tip of optical fibers. This approach opens a new route to functional integrated photonic devices.
ACKNOWLEDGMENTS

With such a multi-disciplinary thesis, I have drawn help from many people. I cannot acknowledge everyone who has helped me in the research of this dissertation. Regardless, without all these amazing people I would never have made such an accomplishment.

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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>2PA</td>
<td>Two-photon absorption</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>3PA</td>
<td>Three-photon absorption</td>
</tr>
<tr>
<td>AR</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Becke’s three parameter exchange, Lee, Yang, and Parr correlation</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled device</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DLW</td>
<td>Direct laser writing</td>
</tr>
<tr>
<td>FCT</td>
<td>Face centered tetragonal</td>
</tr>
<tr>
<td>FROG</td>
<td>Frequency resolved optical gating</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width at half maximum</td>
</tr>
<tr>
<td>GBL</td>
<td>Gamma-butyrolactone</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>ITX</td>
<td>Isopropyl thioxanthone</td>
</tr>
<tr>
<td>IPSF</td>
<td>Irradiance point spread function</td>
</tr>
<tr>
<td>mpDLW</td>
<td>Multi-photon direct laser writing</td>
</tr>
<tr>
<td>PAG</td>
<td>Photoacid generator</td>
</tr>
<tr>
<td>PhC</td>
<td>Photonic crystal</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PEB</td>
<td>Post-exposure bake</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
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<tr>
<td>PGMEA</td>
<td>Propylene glycol methyl ether acetate</td>
</tr>
<tr>
<td>PMT</td>
<td>Photo-multiplier-tube</td>
</tr>
<tr>
<td>PSF</td>
<td>Point spread function</td>
</tr>
<tr>
<td>PZT</td>
<td>Piezoelectric transducer</td>
</tr>
<tr>
<td>RIC</td>
<td>Refractive index contrast</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHG</td>
<td>Second harmonic generation</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>Time-dependent density functional theory</td>
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</tbody>
</table>
LIST OF NUMERICAL PARAMETERS

\( \delta_{2PA} \)  Two-photon absorption probability

\( \delta_{3PA} \)  Three-photon absorption probability

\( \Delta \)  Pulse-to-pulse pitch spacing [nm]

\( \Delta f \)  Measured shift in the geometric focal point [\( \mu \)m]

\( \varepsilon \)  Molar absorptivity [L mol\(^{-1}\) cm\(^{-1}\)]

\( \Gamma \)  Full-width at half maximum of a Lorentzian function

\( \hbar \)  Reduced Planck constant [1.054 \times 10\(^{-34}\) J s]

\( \lambda \)  Wavelength [nm]

\( \sigma^{(n)} \)  Cross-section of \( n \)th order absorption process [cm\(^{2n}\) s\(^{-1}\) photon\(^{n-1}\) molecule\(^{-1}\)]

\( \tau \)  Full-width at half maximum (FWHM) of the temporal envelope of a laser pulse width [s]

\( \omega \)  Frequency of light [s\(^{-1}\)]

\( A \)  Area [cm\(^2\)] or electric field amplitude [V m\(^{-1}\)]

\( C \)  Molar concentration [mol L\(^{-1}\)]

\( d \)  Expected writing depth [\( \mu \)m]

\( E_{p} \)  Laser pulse energy [J]

\( h \)  Planck constant [6.626 \times 10\(^{-34}\) J s]

\( f \)  Oscillator strength

\( f_{\text{rep}} \)  Laser pulse repetition rate [pulses s\(^{-1}\)]

\( F \)  Photon flux [photons s\(^{-1}\) cm\(^{-2}\)]

\( F_{0} \)  Peak photon flux [photons s\(^{-1}\) cm\(^{-2}\)]
I  Irradiance [W cm\(^{-2}\)]

\(I_{pk}\)  Peak irradiance [W cm\(^{-2}\)]

\(n\)  Number of photons absorbed (order of nonlinear absorption) or refractive index

\(N\)  Number density of molecules [molecules cm\(^{-3}\)]

\(NA\)  Numerical aperture

\(N_A\)  Avogadro constant [6.022 \times 10^{23} \text{ mol}^{-1}]

\(<P>\)  Average power transmitted through an objective lens to a sample [W]

\(P_{pk}\)  Peak pulse power [W]

\(P_{avg}\)  Average pulse power [W]

\(r\)  Radial distance from the optic axis center of a focused laser beam [nm or \(\mu m\)]

\(R\)  Resistance [ohms] or radius of curvature [\(\mu m\)]

\(T\)  Temperature [K or °C]

\(T_g\)  Glass-transition temperature [°C]

\(T_{min}\)  Minimum transmittance

\(T_p\)  Fresnel transmission coefficient (p-polarization)

\(T_s\)  Fresnel transmission coefficient (s-polarization)

\(V\)  Volume [cm\(^3\)]

\(r_0\)  Beam waist [nm or \(\mu m\)]

\(z\)  Axial distance from focal center [nm or \(\mu m\)]

\(z_R\)  Rayleigh length [nm or \(\mu m\)]
CHAPTER 1: INTRODUCTION

1.1. General principles

There is an ever increasing need for complex, micron-scale devices, which drives intense research in materials and processes for micro- and nano-scale fabrication [1-3]. Photolithography is a forefront fabrication technique that consists of exposing a photoactive material to light though a mask, forming an exposure pattern [4, 5]. The exposed pattern in the material undergoes a photochemical change, which allows either it or the unexposed regions to be selectively removed via dissolving or etching process (commonly the development process) [4, 5]. This broad class of techniques has enabled routine fabrication of structures with feature resolution in the micro- and well into the nanometer scale [6]. These advances have become possible through the development of new materials and processes that enable continual reduction of the exposure wavelength, from ultraviolet to x-ray, and employing other techniques, such as liquid immersion optical lithography and maskless E-beam lithography [7]. Despite the amazing progress with improving resolution, there is one apparent drawback: these techniques expose one layer of material at a time, which limits the approaches to fabrication of two-dimensional (2D) structures [6]. Although they can be leveraged to make 3D structures with “layer-by-layer” processing, the target structures are necessarily limited in complexity, and their fabrication involves great complexity and increased cost. Thus, the need has steadily grown for a truly 3D fabrication technique that enables structures of arbitrary complexity to be fabricated with ease at low cost. One such technique that has emerged in the past two decades is multi-photon direct laser writing (mpDLW) [8].
In mpDLW a laser beam is tightly focused into a photo-active material that has been deposited onto a substrate (Figure 1.1), such as a polymeric or pre-polymer photoresist [9]. Typically, the material is virtually transparent to the light, so one-photon absorption (1PA) is negligible. However, as the beam focuses inside the material, the irradiance increases and becomes high enough to induce chemical or physical changes via multi-photon absorption processes, such as two-photon absorption (2PA, Figure 1.2) [8]. As distance from the geometric focal point increases, the irradiance decreases, so the rate of absorption is reduced in all directions. As a result, the physical or chemical change that results from nonlinear absorption is tightly confined to a small volume around the geometric focal point. By simply scanning the focal point throughout the material in any direction, a true 3D exposure pattern can be generated point by point, and then developed to reveal a 3D structure that is either a positive- or negative-tone replica of the exposure pattern (Figure 1.3) [10].
Figure 1.1. Illustration of multi-photon direct laser writing (mpDLW). A collimated laser beam is focused into a photoactive material by an objective lens. Photo-modification occurs inside the focal volume where the intensity is high enough to induce non-linear effects such as two- or multi-photon absorption. The targeted 3D photo-pattern is created by scanning the sample relative to the focal point using a 3-axis translation stage.
**Figure 1.2.** Excitation diagram of one-photon absorption (blue arrow) and degenerate two-photon absorption (red arrows). The equivalent excitation achieved by absorption of a 400-nm photon can in principal be achieved by absorption of two 800-nm photons provided the irradiance is high enough and the two-photon optical transition is allowed. The dotted line represents the virtual state intermediate in the two-photon absorption process.

**Figure 1.3.** Post-exposure process after mpDLW: (Left) Photo-patterning by mpDLW; (Middle) Development with a liquid solvent; (Right) Free standing negative-tone structure that results after exposure and development.
1.2. Resolution of multi-photon direct laser writing

1.2.1. Beam characteristics

It is necessary to understand the general properties of a laser beam and how a photo-active material responds to it if we are to understand how a multi-photon absorption process offers increased resolution compared to a 1PA process and how it might be improved. In most applications of mpDLW the laser beam is expanded using a telescope before it is focused using the objective. This is done so that the fractional area of the expanded beam which enters through the back aperture of the objective has a nearly flat phase front and uniform amplitude, which is the condition needed for diffraction-limited focusing to the smallest focal spot achievable with only a single beam and single lens [11]. Under low numerical aperture (NA) focusing, the 3D irradiance distribution around the geometric focus can be calculated using analytic formula. Under high-NA focusing, vector diffraction theory must be used (see Section 2.4.5), and the irradiance distribution must be calculated numerically. To good approximation the irradiance distribution of the most intense lobe in the diffraction-limited focal pattern can be approximated using the equations for focusing of a Gaussian beam (Figure 1.4) [12]. Assuming the beam is aberration free and no absorption is taking place, the radially symmetric irradiance distribution (in units of W cm\(^{-2}\)) of a Gaussian beam as a function of position \(z\) along the optic axis and radial distance \(r\) from the optic axis is given by [13]:

\[
I(r, z) = \frac{2 < P >}{\pi w^2(z)} \exp \left( -\frac{2r^2}{w^2(z)} \right) \tag{1.1}
\]

where \(I_{pk}\) is the irradiance and \(<P>\) is the time-average power transmitted through the objective (in W). The beam radius \(w(z)\) is the distance \(r\) at which the irradiance decreases to 1/e\(^2\) (13.5%)
of its value on the optical axis, $I(r = 0)$. Although this definition is used throughout the dissertation, some parts of the dissertation refers to beam width as the full width at half maximum (FWHM) (the full width of the beam in which its irradiance is at or over 50% of the maximum) which is commonly adopted for the discussion of non-Gaussian beams. The beam radius varies with $z$ as [13]:

$$w(z) = r_0 \sqrt{1 + \left( \frac{z}{z_R} \right)^2}$$  \hspace{1cm} (1.2)

$$z_R = \frac{\pi r_0^2}{\lambda}$$  \hspace{1cm} (1.3)

where $r_0$ is the beam waist located at the focal plane. The Rayleigh range $z_R$ is distance from the focal plane at which the beam radius has expanded to $\sqrt{2} w_0$, so the irradiance has decreased by one half. Using paraxial approximation where rays converge at low angles in respect to the optical axis, $r_0$ can be estimated as [14]:

$$r_0 = \frac{0.61\lambda}{NA}$$  \hspace{1cm} (1.4)

where $NA$ is the numerical aperture of the objective lens. When a Ti:sapphire laser is used as the excitation source, the wavelength is typically 800 nm, as this corresponds to the peak of the laser gain curve and thus the wavelength at which the system is most stable and for which there is the most available power. However, several other excitation wavelengths have been used to pattern SU-8 by mpDLW [15, 16]. Typical high resolution oil immersion objectives have a $NA$ of 1.4.
1.2.2. Material response

In order for the beam to create a change in the exposed area, the material must absorb its energy. The excitation process can be understood by first considering the photon flux \( F = \frac{I}{(\hbar \omega)} \) (in units of photons per unit-area per unit-time) that is incident on a volume containing absorbing species, or photo-initiator molecules in the present case (Figure 1.5). The term \( \hbar \omega \) is the photon energy. The absorption strength of a molecule is characterized using an absorption cross-section, \( \sigma \), which has units of cm\(^2\) molecule\(^{-1}\). The absorbing volume can be viewed as containing a homogenous array of targets of area \( \sigma \) per molecule. The concentration of the absorbers and \( \sigma \) determine the probability that a photon is absorbed and the amount of light that is absorbed by and transmitted through the medium.
Figure 1.5. Photoinitiators absorbing incident light in a photoresist. The photon energy $\hbar \omega$ has units of J.

Under pure 1PA, and assuming negligible down conversion, the rate at which molecules are excited per unit volume per unit time $t$ is [17]:

$$\frac{dN_{ex}}{dt} = \left( \frac{1 \text{ molecule excited}}{1 \text{ photon absorbed}} \right) \sigma N_g F$$

(1.5)

$N_{ex}$ and $N_g$ are the number densities (concentrations) of molecules in the excited state and ground state, respectively, and by convention these have units of molecules per cm$^3$. The fraction in parentheses states that one photon is absorbed for each molecule that is excited. This term is frequently omitted and understood, but is included here for completeness and to permit dimensional analysis. For 2PA, the excitation rate is given by [17]:

$$F = \frac{l(r,z)}{\hbar \omega}$$
\[ \frac{dN_{ex}}{dt} = \frac{1}{2} \sigma^{(2)} N_g F^2 \]  

(1.6)

where \( \sigma^{(2)} \) is the two-photon absorption cross-section, in units of cm\(^4\) s photon\(^{-1}\) molecule\(^{-1}\). The factor 1/2 indicates that one molecule is excited for every two photons it absorbs simultaneously (or within the lifetime of the virtual state)\(^1\), so the 2PA excitation rate is proportional to \( F^2 \).

A generalized expression for the excitation rate under \( n \)-th order absorption is then:

\[ \frac{dN_{ex}}{dt} = \frac{1}{n} \sigma^{(n)} N_g F^n \]  

(1.7)

where the variable \( n \) is the number of photons simultaneously absorbed by the material, or the order of the absorption (OAP), depending on if there are non-resonant processes taking place.

The absorption cross-section of the ground state molecules \( \sigma^{(n)} \) will have units depending on \( n \) and is cm\(^{2n}\) s\(^{-n}\) photon\(^{-n}\) molecule\(^{-1}\).

The implication of the squared dependence of 2PA on incident flux and its usefulness for mpDLW can be appreciated by integrating Equations 1.5 and 1.6 and calculating \( N_{ex} \) as a function of \( r \) in the focal plane (\( z = 0 \)) for both 1- and 2PA. The flux versus \( r \) is obtained from Eqn. 1.1 as

\[ F(r, 0) = \frac{1}{\hbar \omega} \frac{2 < P >}{\pi r_0^2} \exp \left( \frac{-2r^2}{r_0^2} \right) \]  

(1.8)

Other conditions used include \( r_0 = 360 \) nm (determined from Equation 1.4, this is a typical estimate of \( r_0 \) for our system having \( NA = 1.4 \) and \( \lambda = 800 \) nm), \( N_g = 10^{20} \) molecules cm\(^{-3}\), \( \sigma^{(1)} = 10^{-18} \) cm\(^2\) molecule\(^{-1}\) \( \sigma^{(2)} = 10^{-49} \) cm\(^4\) s photon\(^{-1}\) molecule\(^{-1}\). For 2PA the peak photon flux was increased so both reached the same peak value of \( N_{ex} \). The resulting plot is shown in Figure 1.6.
Although the peak excitation density is the same in both cases, in the case of 1PA the FWHM of $N_{ex}$ versus $r$ is $1.2r_0$, whereas it is $0.8r_0$ for 2PA, which means 2PA gives a ~33% narrower excitation region overall.

![Figure 1.6. Plot of $N_{ex}$ as a function of $r$ under 1- and 2PA.](image)

The axial excitation density is similarly obtained, using $r = 0$ and a flux density given by:

$$F(0, z) = \frac{1}{\hbar \omega} \frac{2 < P >}{\pi r_0^2 \left( 1 + \left( \frac{z}{z_R} \right)^2 \right)}$$  \hspace{1cm} (1.9)

The resulting distribution of $N_{ex}$ versus axial position $z$ is shown in Figure 1.7. Again, the improvement is on the order of ~35%.
Figure 1.7. Plot of $N_{ex}$ as a function of axial position. The parameters used are $N_{ex} = 10^{18}$ molecules cm$^{-3}$ and $r_0 = 360$ nm.

Although there is a noticeable increase in resolution with 2PA, high resolution is in principal still attainable via 1PA-DLW [18]. The true benefit of mpDLW is that 2PA (and higher-order absorption) enables excitation to be delivered deeper within the material than is possible by 1PA. Shown in Figure 1.8 is a diagram of the net excitation of molecules within a given focal depth. 1PA scales linearly with photon flux, so the net excitation is invariant throughout the depth of the material, and the beam is steadily attenuated with focal depth. This limits the achievable focal depth of the beam and potential complexity of 3D structures that can be created by lithography based on 1PA. With 2PA, the beam is more selectively absorbed near
the geometric focus. Away from the focus, the absorption rate drops more rapidly compared to the one-photon case [19]. This means that the beam experiences less attenuation than 1PA and more of its focused energy can be delivered deeper into the sample, which enables the exposure of complex 3D patterns in thick photoresist films.

**Figure 1.8.** Net excitation per transversal plane versus axial position for both one-photon (dashed line) and two-photon (solid line) absorption (the beam shape and focus is shown above for convenience). For one-photon absorption the net excitation is constant while for two-photon absorption it is localized near the focal plane.

Direct laser writing has been used to fabricate a variety of 3D microstructures and devices. Photonic crystals of various lattice designs have been fabricated [20-25]. Buried microchannels were fabricated in a positive tone photoresist system [26]. Large aspect ratio (AR)
optical gratings with line widths smaller than the diffraction limit have also been fabricated [19, 27]. Other structures fabricated by mpDLW include gear wheels tapered waveguides, and cantilevers [28, 29].

1.3. Chemistry of materials upon exposure

When a photoresist is exposed to light, it undergoes a series of chemical reactions that modify the structure of the material in the exposed regions. Post-exposure processing, such as wet-chemical etching can be used to remove the exposed material, or vice versa, depending upon the photo-chemistry involved and properties of the etchant used. Several reviews covering the broad range of chemistry, including the photochemistry of custom photoinitiators used for mpDLW have been published [30, 31]. There are generally two types of photoresists, identified as "negative-tone" and "positive-tone", depending on which region dissolves away in the developer. If the exposed material dissolves away, then the process is referred to as positive-tone. If the unexposed material dissolves, then the process is called negative-tone. Arguably, most materials that can be used for conventional lithography could also be used for mpDLW. This includes liquid acrylates that polymerize by radical-initiated polymerization and cross-linking [32-34]. This class of polymer is favored for its rapid polymerization rate and high speed. There are also liquid or solid epoxides (including one that is the subject of this dissertation) that polymerize by cationic ring opening polymerization [15]. The solid resists are favored for their stability during patterning. There are also inorganic-organic hybrids [35-37], some of which are composed of siloxane backbones with pendant organic side groups. While negative-tone resists are used more often, there are several cases of positive-tone resists being used in mpDLW. One example is a copolymer of tetrahydropranyl and methyl methacrylate that
chemically cleaves into carboxylic acid moieties (rendering the polymer soluble in aqueous solvents) in the presence of acid [26]. It should be mentioned that dielectrics such as glass can also be machined and processed as a positive-tone material in mpDLW [38, 39] because the absorption mechanism can involve the simultaneous absorption of photons delivered by a focused laser beam.

Along with the matrix material, there is a broad range of photoinitiators, solvents, and additives which have been applied for mpDLW. The advantages of highly efficient initiators with high multi-photon absorption strengths have been well discussed in literature [26, 40-46]. Although these custom photoinitiators ultimately afford faster fabrication and less needed laser power (cheaper lasers can be used), they are somewhat offset by their multi-step synthesis and cost. Two-photon sensitizers which absorb the light and transfer its energy to an accepting photoinitiator have been explored [22, 47]. Metal salts that can be loaded well into the ~50 wt-% range and reduced to nanoparticles in the polymer matrix have been demonstrated [48]. These are just a few of the materials that have been used to demonstrate mpDLW, and more are expected to become available in the future.

1.4. Using SU-8 as a material for multi-photon direct laser writing

1.4.1. General properties of SU-8

SU-8 is a negative photoresist developed by IBM in the late 1980’s, based on the EPON resin by Shell Chemical and now marketed by MicroChem Corporation [49-51]. A review of the resist used in various fabrication techniques was given [52]. The main components of the currently available SU-8 are shown in Figure 1.9. The photo-crosslinkable component is oligomers of glycidyl-functionalized bisphenol A. The average number of repeat units per
oligomer is four, although gel permeation chromatography has shown a wider distribution of oligomer chain length being present [53]. The bridging methylene is always attached at the ortho position relative to the glycidyl groups but is random between the two possible aromatic rings of each bisphenol A fragment. The oligomers are blended with a mixture of two photoacid generators (PAGs, Figure 1.9) which are 4-(phenylthio)phenyldiphenylsulfonium hexafluoroantimonate (referred to hereafter as "mono-sulfonium", CAS# 71449-78-0) and bis[4-(diphenylsulfonio)phenyl] sulfide hexafluoroantimonate (referred to hereafter as "bis-sulfonium", CAS# 89452-37-9). Other components in the resist include cyclopentanone and propylene carbonate, which are solvents for the resist and the PAGs, respectively, that are included at varying amounts to control the viscosity for spin coating the SU-8 into thin films. In Figure 1.10 is a proposed mechanism of photoacid generation from mono-sulfonium (which may apply for bis-sulfonium) and Figure 1.11 is a general mechanism of the SU-8 cross-linking. Upon photoexcitation, the sulfonium PAGs undergo a series of reactions that ultimately yield Brønsted acid, among other products [54-56]. With a post-exposure bake, the acid cross-links the epoxide oligomers via cationic initiated polymerization [57].
Figure 1.9. Primary components of SU-8: (Left) SU-8 oligomer and (Right) the sulfonium PAGs 4-(Phenylthio)phenyldiphenylsulfonium hexafluoroantimonate ("mono-sulfonium") and bis[4-(diphenylsulfonio)phenyl] sulfide bis(hexafluoroantimonate) ("bis-sulfonium").
Figure 1.10. Proposed mechanism for Brønsted acid generation by irradiation of PAGs. RH depicts a proton donor (such as water, solvent, or monomer) [54-56].
Figure 1.11. General mechanism of SU-8 cross-linking. In the first step, mono-sulfonium yields acid H\(^+\) upon photoexcitation. In the second step, H\(^+\) protonates an epoxy moiety of SU-8 oligomer, generating a carbocation. The carbocation reacts with the epoxide of another SU-8 oligomer and this process continues producing a long polymer chain and/or cross-link network [57].

SU-8 has been extensively used for conventional lithography and has been used as a polymeric material for mpDLW [15, 19, 21-24, 48, 58-62]. First, it readily absorbs in the deep UV, but is virtually transparent at longer wavelengths, which insures that at near infrared wavelengths the resist will have negligible one-photon absorption [15]. Second, SU-8 is glassy solid and mechanically stable during exposure. Also during exposure, there is little change in refractive index so there is little change to the focus when it goes through exposed regions. This is arguably better suited than liquid resists which require a more careful exposure pattern to
avoid features from floating away or distorting the focus. Third, the cross-linking of SU-8 is initiated and propagated by a cationic ring-opening mechanism, so it is not as affected by the presence of atmospheric oxygen as compared to the acrylate family of photoresists [63]. Finally, the shrinkage of the material is relatively low (~7%) compared to other photoresists [52, 64]. Along with the high degree of cross-linking, chemical and thermal resistance, these advantages make SU-8 a highly preferred photoresist for mpDLW.

1.4.2. Impact of processing conditions of SU-8 in multi-photon direct laser writing

In order to fully realize the potential of SU-8 photoresist in mpDLW, the effect of the processing conditions must be understood and controlled. Figure 1.12 is a diagram of the processing steps of the fabrication of SU-8 microstructures with both mpDLW and conventional 2D lithography. The processing can be divided into four steps: (1) preparation of an SU-8 film; (2) exposure of the film to light; (3) post-exposure bake to promote cross-linking of the exposed SU-8 regions; and (4) development of the completed microstructure. Each step has key processing parameters, such as pre-exposure bake time, exposure power, and post-exposure bake (PEB) temperature. Although the main difference between mpDLW and conventional lithography is in the exposure step, two important differences should be appreciated. The first is that features produced by mpDLW are typically patterned at irradiances just above its threshold in order to maintain the highest possible resolution. Microstructures made from mpDLW are found to have mechanical properties that are significantly different than those made in conventional lithography, which can be attributed their lower cross-link densities [65]. The exposure patterning is inherently 3D, so exposure, reaction, and diffusion models developed for 2D lithography are not necessarily applicable to mpDLW. Processing steps previously
understood in conventional lithography can have a different effect in mpDLW. For example, the low cross-linked features of structures in mpDLW are more susceptible to development shrinkage [53]; and the sharper gradient of photoacid density generated by mpDLW can result in higher amounts of acid diffusion in the PEB step. The second is that there are conditions that are unique to mpDLW, such as writing depth, and scan speed. There is much interest in exploring the large number of processes that can occur or be controlled in mpDLW processing [66-69]. Understanding more about these parameter effects on mpDLW, further increases the applicability of SU-8 in mpDLW, and helps in the long term development of advanced and inexpensive photoresist formulations for mpDLW.

**Figure 1.12.** Process flow of SU-8 fabrication with conventional lithography (left) and multi-photon DLW (right).
1.5. Overview of dissertation

The purpose of this doctoral research was to observe the effects of certain mpDLW processing conditions on feature size and microstructure quality. Typical test structures used in the research are single lines suspended by walls, photonic crystals, and microlenses. Chapter two will detail the general processing methods and controls used to fabricate SU-8 microstructures, and equipment used to characterize the material and structures.

Chapter three details the effect of SU-8 processing parameters on structure fidelity. Although this is well studied in the context of conventional photolithography, it is far less well understood in terms of mpDLW. This chapter provides qualitative and quantitative evidence of how these processing conditions affect outcomes in mpDLW using SU-8.

Chapter four describes how SU-8 feature size is affected by varied writing depth and exposure power. When there is refractive index mismatch between the objective (immersion oil) and the material, spherical aberration results. Although the index mismatch of SU-8 and the immersion oil used here is small (+0.08), the impact is significant, and it is shown that both the line width and height can either increase or decrease, depending on the writing depth and the exposure power. A model of the aberrated focus using vectorial diffraction level of theory is used to quantitatively analyze the observations. Controlling average power is shown to be a useful means to compensate for the effects of refractive index mismatch.

Chapter five describes how feature size is affected by scan speed and exposure power. An analytical model was used to interpret the results and show that SU-8 is photo-activated by three-photon absorption (3PA) at 800 nm. Expanding on this finding, other laser parameters were varied, such as wavelength, which show that the SU-8 photo initiators can be activated by
2PA, 3PA or a combination of both, depending on the laser conditions. Some of these findings are supported by Z-scan measurements of the PAG mixture and quantum calculations of the 2PA and 3PA spectra of the PAG molecules.

Chapter six shows how knowledge of the relationship between mpDLW processing can be applied to create functional devices. Micro-optics were fabricated onto the tips of optical fibers, creating functional integrated photonic devices, and their optical properties were characterized. Chapter seven reviews the potential impact of this work and outlines additional investigations that could extend this work further.
CHAPTER 2: EXPERIMENTAL METHODS

2.1. Fabrication using SU-8

2.1.1. SU-8 film preparation

Microscope slides (Fisher Scientific) were used as substrates for all mpDLW unless otherwise stated. Slides were cut into 19 × 19 mm squares and sonicated in water for 40 minutes at 50 °C and rinsed with water. The slides were then immersed in 1 M KOH(aq) for 30 minutes, rinsed again with water, and dried in an oven at 100 °C for at least two hours. In dark room conditions, 1.5 mL of SU-8 2075 (MicroChem) was dispensed with a disposable pipet on a slide loaded on a SCS/G3P-8 spin coater (Specialty Coating Systems). The coating recipe used vary depending on desired thickness, however the following spin coat recipe has produced films of 40 μm thickness (or 20 μm film when SU-8 2035 was used): (1) 3100 rpm, 31 second ramp, 60 second dwell (2) 0 rpm, 10.3 second ramp. Two hotplates were preheated to 65 °C and 95 °C, and the films were baked with the following recipe: (1) 65 °C for 15 minutes (2) 95 °C for ~14 hours (3) 65 °C for 15 minutes.

2.1.2. Exposure process

In Figure 2.1 is a diagram of the mpDLW apparatus. The SU-8 coated slides were mounted onto a three-axis nanopositioner (Physik Instrumente 563.3CD) and affixed to an inverted microscope (Nikon TE2000-U). The laser used was a continuous-wave mode-locked Ti:sapphire laser (Coherent-Mira, 800-nm center wavelength, 120-fs pulse duration, 76 MHz laser pulse repetition rate). Power from the laser was controlled with a half-wave plate and Glan-Thompson polarizer. A portion of the beam was directed onto a photodiode that provided a
continuous relative measure of the laser output power, while the average power outputted from
the objective was measured using a calibrated integrating sphere (Optronic Labs). The
integrating sphere was calibrated for each wavelength against a calibrated power meter head
(Newport 883-UV). Another portion of the beam was directed into a GRENOUILLE single-shot
pulse measurement system (Swamp Optics, http://www.swampoptics.com) that permitted
continuous monitoring of the laser pulse spectrum and temporal profile. The system uses a
simplified version of frequency resolved optical gating (FROG) in which the beam is split in two
by Fresnel biprism and crossed inside a thick second harmonic generation (SHG) crystal [70].
The system gives the temporal profile of the pulse and the FWHM pulse duration.

The laser beam was expanded with a telescope and directed into a 60×/1.4-NA Plan Apo
oil-immersion objective lens (Nikon Type A oil, n = 1.51 at 800 nm) such that it overfilled the
back aperture. The beam profile of the expanded beam was measured and found to be uniform to
within 5% across the lateral width of the back aperture (5.6 mm). These conditions yield a
diffraction limited irradiance distribution at the focus [11].
Figure 2.1. Diagram of the DLW fabrication apparatus. The laser beam was expanded to overfill the back aperture of a high-NA objective. Electronic shutter and nanostage were synchronously controlled by a computer. Reflection images from the sample were collected by the camera.

The SU-8/oil and SU-8/glass interfaces were located by imaging the reflection of the laser beam with a CCD camera. After locating the interfaces, patterning was achieved by synchronous control of the electronic shutter and nanostage by a computer. The exposure pattern was composed of line segments written in a text file that was executed by LabView software that simultaneously controls the nanostage and the shutter.

The scan speed of the nanostage can ranged from 1 to 800 $\mu$m s$^{-1}$. Because of the mass of the stage, the device has a finite acceleration, which means that the instantaneous scan speed can deviate from the target scan speed. To measure scan speed at various points in a line scan, the
nanostage was commanded to write line patterns at a range of targeted speeds during which the position versus time was monitored by an oscilloscope. The voltage signal from the nanostage position sensors (used as a feedback signal for the servomechanism of the nanostage) was channeled by a BNC cable to the oscilloscope. A calibration of sensor voltage versus targeted position was measured (Figure 2.2). Waveforms of sensor voltage as a function of time were recorded for each line segment to obtain plots of the actual position versus commanded position. An example waveform is shown in Figure 2.3. The instantaneous slope of the waveforms gave the speed of the state at a given point during the line scan. This type of measurement was used to study the acceleration-profile and average speed achieved when the nanostage was commended to move at a given speed.

![Figure 2.2. Plot of nanostage position sensor voltage as a function of targeted nanostage position (x-axis).](image)
Figure 2.3. Waveform of nanostage capacitance sensor output (voltage versus time) when commanded to move at 6.25 μm s⁻¹. The beginning of the scan and the corresponding change in speed is depicted by the red arrow.

2.1.3. Post-exposure process

Following exposure, the sample holder was taken out, and the sample was removed. Objective oil was wiped off the film surface a dry lens cleaning tissue. The samples were then baked to promote cross-linking of the exposed regions. Using two hotplates, the samples were heated using the following profile: (1) 65 °C for 1 minute, (2) 95 °C for 15 minutes (3) 65 °C for 1 minute. The baked samples were immersed in propylene glycol methyl ether acetate (PGMEA,
CAS# 108-65-6) for 20 minutes to dissolve away the unexposed regions. The samples were rinsed with PGMEA, isopropyl alcohol (IPA), and gently air dried.

The temperature of the hotplate or a thick film of SU-8 was measured with a small bead thermistor (Redfish Sensors, PicoBead 10K ± 20%, Part RPBA-103M-35). The thermistor was soldered to a voltmeter and calibrated by immersing it various solvents heated to boiling (see Table 2.1). The temperature of the solvents boiling point was plotted as a function of the recorded resistance of the immersed thermistor and fitted to the Steinhart-Hart equation:

\[
T = \frac{1}{A + B \ln(R) + C (\ln(R))^3}
\]  

(2.1)

where \(T\) is the temperature in K, \(R\) is the recorded resistance in ohms, and \(A, B,\) and \(C\) are fitting parameters. An example fit is given in Figure 2.4. The error of the fit is approximately 0.6%.
Table 2.1. List of solvents used for thermistor calibration.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling Point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-xylene</td>
<td>417.35</td>
</tr>
<tr>
<td>1-butanol</td>
<td>390.35</td>
</tr>
<tr>
<td>trichloroethylene</td>
<td>360.35</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>404.15</td>
</tr>
<tr>
<td>toluene</td>
<td>383.75</td>
</tr>
<tr>
<td>water</td>
<td>373.15</td>
</tr>
</tbody>
</table>

Figure 2.4. Plot of solvent boiling point as a function of the measured resistance.
2.1.4. *SU-8 fabrication using an amplified femtosecond laser source*

Sample preparation and optical setup is as described in the previous sections with the following differences. Seed pulses from a mode-locked Ti-sapphire laser operating at 800 nm (Mira, Coherent) were taken to a regenerative amplifier (Coherent Legend Elite; FWHM pulse width ~90 fs; FWHM bandwidth ~ 10 nm; pulse repetition rate = 1 kHz), and spatially filtered through a 75-μm pinhole. The sample and nanostage were affixed to a mobile fabrication apparatus which consists of similar, if not the same, components as those used in the standard process. The scan speeds used with the AFS were 1 to 128 μm s⁻¹. The average power used under this system was 0.1 to 2 μW.

2.2. *Fabrication of micro-structures on the tip of optical fibers*

A 50-mL round bottom flask was filled with ~10 mL of SU-8 2075. The flask was placed in a rotary evaporator equipped with a dry vacuum and heated to 95 °C to evaporate the cyclopentanone solvent. The pressure was gradually lowered to ~9 Torr to prevent foaming and maintained for at least 30 minutes. The round bottom flask was then connected to a vacuum manifold with an oil vacuum pump which gave a pressure of < 0.5 Torr. Heating was continued for ~14 hours. Using a heat gun to maintain temperature (the resin instantly solidified when cooled), the molten resin was poured into a glass plate and allowed to cool. The hardened resin was then broken into small pieces (around 0.5 cm) and stored in the dark.

The optic fibers used were single-mode fibers (Nufern/ThorLabs, 630 HP, core diameter 3.3 μm ± 0.1 μm, core and clad refractive index 1.463 and 1.457 at 633 nm, respectively). Around 1-cm of the plastic jacket was removed by shearing off a portion with a razor blade,
immersing in acetone for 30 seconds to swell the jacket, and then removing the jacket segment by hand. A flat and clean fiber edge was created by scribing a small indentation on the side of the fiber with a diamond scribe and gently snapping off the end by pressing on the tip. The quality of the end face was checked with an optical microscope.

Solvent-free SU-8 was melt-reflowed (dry chip casted) into a SU-8/fiber optic sample holder (Figure 2.5). The sample holder consists of a fiber optic chuck attached to a single axis micrometer that allows the fiber to be lowered into a solid SU-8 well 5 mm wide and 1 mm high. A coverslip was attached to the bottom of the well and the fiber was aligned and lowered 50 μm from the coverslip. The coverslip was removed and the sample holder was placed over a coverslip-on-hotplate preheated to 110 °C. Pieces of the solid SU-8 were loaded 1-2 pieces at a time (without disturbing the aligned fiber), melt-reflowed around the fiber, and repeated until the well is sufficiently filled. The hotplate was turned off and the SU-8 was allowed to solidify and cool. After the resin hardened, the coverslip was gently removed from the sample holder and the entire unit was affixed to the nanopositioner used in the standard SU-8 fabrication.
Figure 2.5. (A) Optical fiber and SU-8 resin mould. (B) Melt-reflow process. (C) Images of the SU-8 melting and reflowing, with embedded fiber (white line in center of image).

The fabrication system used to fabricate structures on the end face of fibers is exactly as described in Section 2.1.2. The main difference is that the end-face of the fiber served as the substrate upon which the free-standing micro-structure is fabricated. Light from a HeNe laser (632 nm) was coupled into the free end of the fiber and imaged as it emerged from the core of the opposite end which is affixed in the solidified SU-8. This light was observed through the microscope during positioning of the sample so that the center of the core can be located and used to reference the start-position for fabrication of the microstructure. The typical average power used here was 2.4 to 3.0 mW at a scan speed of 50 \( \mu \text{m s}^{-1} \). After patterning, the sample holder was detached from the nanostage and placed polyimide film laying atop a hotplate to bake
the photo-patterned resin for 15 min at 105 °C. The sample was transferred to cold surface and allowed to cool for 5 min, then developed in PGMEA for ~1 hour, rinsed with PGMEA/IPA and allowed to dry in air.

Figure 2.6. System used to fabricate microstructures on the tip of an optical fiber.
2.3. Photoresist characterization

2.3.1. Measurement of SU-8 film thickness

The resulting thickness of the films was measured in one of four ways. In the first method, selected films were cracked through the center (substrate included) and the side view profile of the film was imaged by scanning electron microscopy (SEM TE-SCAN, 10 kV accelerating voltage). In the second method, a pit was carefully made in the center of representative films with a sharp object and a stylus profilometer was scanned across the pit which gives the depth of the film. This method is helpful for quick measurement of the surface profile of the film. The third method was performed immediately before patterning. The focus was positioned by moving the nanostage vertically (along the z-axis, see Figure 1.1) while monitoring the reflection of the laser beam from the sample. When the beam focused at an interface, the refractive index mismatch gave a larger reflection, which is essentially an image of the focused irradiance distribution in that plane. The relative distance travelled along the z-axis was noted between location of the (1) objective-oil/SU-8 interface (the surface of the SU-8 film), and the (2) SU-8/substrate interface. The distance from one interface to the other is approximately the thickness of the film, with a systematic error that was found to be approximately +10% due to refractive index mismatch between the objective oil and SU-8 (for more detail, see Ch. 4, p. 90). In the final method, the microstructure walls were patterned in a height that exceeds the thickness of the SU-8 film, resulting in the entire depth of the film being exposed. From side view SEM images, the height of the resulting structure corresponds approximately to the thickness of the film, with a systematic error that results from unavoidable shrinkage of the material.
2.3.2. Measurement of refractive index of SU-8 films

The refractive index of the spin coated and pre-baked film was determined by rotational shift of interference pattern [71]. The procedure consists of collecting UV/visible transmission spectra of a thin film as it is rotated relative to the incident optical beam. Fringes at wavelengths \( \lambda_0, \lambda_1 \ldots \lambda_i \) appear in the UV-Vis spectrum due to standing wave interference and are progressively shifted by rotation of the film (Figure 2.7). The overlap angle \( \phi_{\lambda x} \) is the angle in which the wavelength of the shifted fringe \( \lambda_0 \to \lambda_i \) is the same as its neighbor (toward the blue) extreme \( \lambda_1 \) observed at normal incidence (Figure 2.8). The variables \( \lambda_0, \lambda_1, \) and \( \phi_{\lambda x} \) were used to determine the refractive index at \( \lambda_1 \):

\[
\frac{\lambda_0}{\lambda_0 - \lambda_i} = j_1
\]

where higher values of \( i \) refer to fringes at shorter wavelengths. The data was fitted to a 1st order Cauchy equation which was then interpolated to determine the refractive index \( n(\lambda) \). A photodiode array spectrophotometer (Agilent 8453) was used for these measurements with a home-built rotation stage and sample mount. The refractive index of a film up to ~2 \( \mu \)m film can
be determined; however, thicker films could not be analyzed using this method because the fringe spacing increased with thickness beyond the spectral range available with the spectrophotometer.

**Figure 2.7.** Example UV-Vis spectra of a thin SU-8 film taken at various incidence angles. Two extrema are chosen at normal incidence (arrows 1 and 2) corresponding to wavelengths $\lambda_1$ and $\lambda_0$. The incident angle $\phi$ is increased until $\lambda_0(\phi)$ is shifted (arrows 3-5) to overlap with $\lambda_1(\phi = 0)$. 
Figure 2.8. Plot of the fringe-overlap as a function of incidence angle. The overlap angle $\phi_{vx}$ where $\lambda_{\phi} - \lambda_0 = 0$ is indicated with the black arrow.

Figure 2.9. Example dispersion curve acquired from rotational shift of interference patterns of SU-8.
2.3.3. Solvent content of SU-8 film

$^1$H-NMR was used to determine the solvent content of processed SU-8 films. After pre-baking a film, the remaining material was scraped off the substrate and transferred to a scintillation vial. One mL of deuterated chloroform containing tetramethylsilane as an internal reference was added and allowed to dissolve the material. The solution was then filtered and loaded into a 5-mm bore NMR tube. Reference spectra were obtained individually for each of the solvents and SU-8 oligomer alone (solids free of PAG or solvent, MircoChem) by similarly dissolving mg quantities of the compounds in CDCl$_3$ and recording the $^1$H-NMR spectrum. By comparing spectra of the processed resin with that of the neat solvents, it was determined that chemical shifts 6.4 - 7.2 ppm (complex multiplet) correspond to aromatic protons of the SU-8 oligomers, and those in the range 1.8 – 2.3 ppm (pair of roofed multiplets) correspond to the cyclopentanone solvent. Standards were made consisting of known amounts of EPON SU-8 (dry SU-8 oligomers without solvent and PAGs) and cyclopentanone solvent which are used to make a calibration curve that relates the ratio of the two integrated signals to the relative mass of the solvent and oligomer. The solvent content of the SU-8 resist is defined as:

$$w_{solvent} = \frac{m_{solvent}}{m_{solvent} + m_{oligomer}}.$$  \hspace{1cm} (2.4)$$

where $w_{solvent}$ is the mass percent of the solvent, and $m$ is the mass of the particular component. The mass of other components, such as propylene carbonate and photoinitiator, are not included in the definition, but the values should be comparable to those obtained gravimetrically because the oligomer constitutes more than 90% of the film after processing.
2.3.4. Composition of the PAG mixture

Sulfur and fluorine mass analysis was used to determine the molar ratio of mono- and bis-sulfonium in the PAG mixture. Attempts to separate and quantify the PAG components by chromatography and/or NMR were unsuccessful. A sample of the PAG mixture purchased from Aldrich and a sample of SU-8 2075 from MicroChem were sent to Galbraith Labs for mass analysis. The fluorine content was analyzed using oxygen flask combustion/ion selective electrode. A 1 mg to 200 mg of the sample was placed in a heavy wall oxygen flask and the concentration of fluorine ions was read the ion selective electrode. Stock solutions of NaF were used to make calibration standards. The sulfur content was analyzed using a LECO SC-432DR (a commercial sulfur analyzer). Approximately 150 mg of sample was combusted at 1350 °C in an atmosphere of pure oxygen, oxidizing the sulfur to sulfur dioxide, which was measured by infrared absorption. Various sulfur standards (NIST Bovine Liver, NIST Oyster Tissue, and milk powder) were used for calibration. The mole fraction of the bis-sulfonium, $x_{\text{bis}}$, was given by:

$$x_{\text{bis}} = \frac{-6}{n_F - 6}$$

$$n_F = \frac{w_F}{M_F}, n_S = \frac{w_S}{M_S}$$

where $n_F/n_S$ is the molar ratio of fluorine to sulfur; $M_F$ and $M_S$ are the atomic masses of fluorine and sulfur, respectively; and $w_F$ and $w_S$ are the mass fractions of fluorine and sulphur, respectively, as reported by Galbraith Labs. Equation 2.3 was derived assuming a 1:1 ratio of
hexafluoroantimonate anion and sulfonium cation, and the PAG mixture is the sole source of the sulfur and fluorine. Based on provided uncertainties of the elemental analysis, the propagated uncertainty of $x_{\text{bis}}$ is in the order of 10%.

2.3.5. Z-scan of PAG mixture

The nonlinear absorption of the PAGs was measured by open-aperture Z-scan (see Figure 2.10) [72, 73] using commercially available mixed triarylsulfonium hexafluoroantimonate salts dissolved propylene carbonate (Aldrich, 50 wt-%). The laser source used was the AFS (Section 2.1.4) adjusted to a pulse repetition rate of 50 Hz. The laser beam was directed to a 150-mm focal length lens mounted on a translation stage. The lens focused the beam into a flow cell through which the PAG was continually circulated at a flow rate of 0.3 mL s$^{-1}$. The lens generated at Gaussian focus with $z_R = 2.5$ mm and a beam waist of $w_0 = 20$ μm at $z = 0$ mm (the center of the Z-scan). The average power in the beam $<P>$ was measured using a calibrated power meter. The focus was scanned through the sample by moving the lens in 0.45-mm steps while the normalized transmittance through the sample was recorded at each $z$-position. Because Z-scan is a nonlinear optical technique, shot-to-shot fluctuations in laser pulse energy can lead to undesirably large deviations in the measured signal. A reference detector was used to measure the relative energy of each laser pulse. The shot-to-shot variation in pulse energy was circa 2%. A pulse-energy gating procedure was used in software to collect data using only those pulses that fell within a narrower pulse-energy bandwidth of ±0.2%. The minimum transmittance ($T_{\text{min}}$, corresponding to transmission measured at the center of the Z-scan) was recorded from each scan. A plot of $\log(T_{\text{min}})$ versus $\log(<P>)$ was made which is expected to yield a straight line,
particularly when a single nonlinear absorption mechanism dominated the light-matter interaction. A best fit of the line was yielded the slope $m$ and the order of the absorption was calculated as $n = m + 1$.

**Figure 2.10.** Diagram of the open aperture Z-scan setup used to measure the nonlinear absorption of PAGs. All of the light that passes through the sample is collected by the sample detector, so a drop in relative transmittance (compared to the reference detector) is due to absorption of the sample. The nonlinear absorption of the sample (assuming negligible linear absorption) is studied by scanning the focus through the sample which modulates the incident irradiance.

To determine the 2PA cross-section, the open aperture Z-scan trace is fitted to the equation:

$$
\Delta T(z) \approx \frac{q_0}{2\sqrt{2}} \frac{1}{1 + \frac{z^2}{z_R^2}}
$$

(2.7)
\[ q_0 = \beta I_0 L_{\text{eff}} \]  \hspace{1cm} (2.8)

\[ \sigma^{2PA} = \frac{\hbar \omega \beta}{N_A \rho \times 10^{-3}} \]  \hspace{1cm} (2.9)

where \( \beta \) is the 2PA coefficient, \( I_0 \) is the incident peak-irradiance, the effective path length \( L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha \) is the attenuation coefficient in units of cm\(^{-1} \), \( \hbar \) is the reduced Planck constant, \( N_A \) is the Avogadro constant, and \( \rho \) is the molecular molar concentration.

2.3.6. Two-photon and Three-photon absorption theoretical calculation of mono- and bis-sulfonium PAGs

The theoretical details for the 1PA, 2PA, and 3PA calculation have been previously described [74-79]. The geometry of the molecular structures of the PAG molecules was optimized by density functional theory (DFT) in Gaussian 09 [80], using the Becke’s three parameter exchange and Lee, Yang, and Parr correlation (B3LYP) hybrid functional [81-83], and 6-31**G** basis set [84] considering solvent effects (DMSO) under the polarizable continuum model (PCM) [85, 86]. The 1PA and degenerate 2PA/3PA response for each of the PAG molecules was calculated using time-dependent DFT [87], using Gaussian 09 for 1PA, and Dalton 2011 [88] for 2PA/3PA. The 1PA spectrum was calculated under PCM, but 2PA/3PA response could only be calculated \textit{in vacuo} because the use of solvent models proved to be too difficult given current computational resources. The basis sets used for the TD-DFT are B3LYP/6-31G* [89].
Table 2.2 lists the number of excited states calculated for the mono-sulfonium and bis-sulfonium molecules for the 1PA, 2PA, and 3PA processes.

Table 2.2. Number of calculated excited states for the PAG molecules.

<table>
<thead>
<tr>
<th></th>
<th>Mono-sulfonium</th>
<th>Bis-sulfonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1PA</td>
<td>160</td>
<td>300</td>
</tr>
<tr>
<td>2PA</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>3PA</td>
<td>15</td>
<td>20</td>
</tr>
</tbody>
</table>

The calculation yielded absorption probability or oscillator strength for each $f_{th}$ excited state having zero bandwidth. To simulate a continuous spectrum, each of the excited states was assumed to undergo heterogeneous line broadening described by a Lorentzian distribution:

$$g(2\omega, \omega_{gf}, \Gamma_{gf}) = \frac{1}{\pi} \frac{\Gamma_{gf}}{2} \frac{1}{(\omega_{gf} - 2\omega)^2 + \left(\frac{\Gamma_{gf}}{2}\right)^2},$$

(2.10)

where $\omega_{gf}$ is the frequency corresponding to the $f_{th}$ calculated excited state, $\omega$ is the frequency of the incident photons, and $\Gamma_{gf}$ is the FWHM of the distribution. The value of $\Gamma_{gf}$ is empirically chosen to best reproduce the experimentally obtained spectra and typically corresponds to a value of 0.2 eV. The distributions for each of the excited states were summed together in the following formula for the 2PA case:
\[ \sigma^{(2)}(\omega) = \frac{4\pi^3 \alpha_0^5}{c} \sum_f (\hbar \omega)^2 \delta^{2PA}_f \left( \omega_{gf} \right) g \left( 2\omega, \omega_{gf}, \Gamma_{gf} \right), \]  

(2.11)

where \( \delta^{2PA} \) is the two-photon cross-section considering the contributions of all the broadened excited states, \( \alpha_0 \) is the fine structure constant, \( a_0 \) is the Bohr radius, and \( c \) is the speed of light.

The 3PA response of the PAG molecules, was computed with Dalton 2011 using a TD-DFT implementation described by Cronstrand et al. [78]. Equation 2.9 was modified for the 3PA case:

\[ \sigma^{(3)}(\omega) = \frac{4\pi^3 \alpha_0^8}{3c^2} \sum_f (\hbar \omega)^3 \delta^{3PA}_f \left( \omega_{gf} \right) g \left( 3\omega, \omega_{gf}, \Gamma_{gf} \right), \]  

(2.12)

2.4. Structure/feature characterization

2.4.1. Scanning electron microscopy

Microstructures fabricated by mpDLW in SU-8 were characterized by scanning electron microscopy (SEM). Accuracy of the SEM imaging system was confirmed by SEM imaging of a microscope calibration target (MetroChip, MetroBoost). Prior to imaging, the structures were sputter-coated (Emitech K550) with a ~20-nm-thick film of Au/Pd to make them electrically conductive. The coating was applied at three angles (normal, and ± 60°) to minimize the effects of surface charging with 3D structures. The samples were imaged normal- and parallel to the substrate to enable measurement of the height and width of microfabricated features, particularly suspended lines created by single-exposure line scans. The uncertainty of the line-width and height measurements is 50 nm and 90 nm, respectively (±1 σ). This variation is found to be mostly dominated by repeated fabrications under the same conditions. Individual lines were
imaged and measured in five different locations at 90,000× magnification (view field ~2.5 μm) to obtain an average line width and its standard deviation.

2.4.2. Optical characterization of microlenses on optical fibers

The optical performance was characterized for fibers upon which micro-optics had been fabricated by mpDLW in SU-8. The spatial irradiance profile was measured using a beam profiler (WinCamD, DataRay) outputted from (1) a fiber bearing a planar convex lens, (1) a fiber bearing a cylindrical lens, and (3) a bare fiber, for comparison. Light from a HeNe laser (633 nm) was coupled into the free, un-functionalized end of the fiber. The beam emerging beam from the opposite end was imaged as a function of distance from the fiber end-face (Figure 2.11). The beam radius, \( w(z) \), along the \( x \)- and \( y \)-axes was measured by fitting the measured irradiance profile to a Gaussian function. The empirical function \( w(z) \) for the far field was used to obtain the beam divergence angle. The fiber bearing the cylindrical lens was pre-oriented with the fast axes parallel to the \( x \)-axis.
Figure 2.11. Example beam profiles obtained at selected distances $z$ from the fiber end-face of an optical fiber containing a plano-convex lens ($R = 18.3 \, \mu m$). Irradiance line-profiles like that shown in $z = 15 \, mm$ were measured along the $x$- and $y$-axis to determine $w(z)$ of the beam.

The propagation of light emerging from microlens-tipped fibers was calculated by $q$-transformation of Gaussian beams, which uses a paraxial Gaussian beam approximation [90]. The calculations include an input wavelength of 633 nm, and index of refraction of 1.463 and 1.592 for the core and SU-8 [91], respectively. The $1/e^2$ beam radius immediately after the end face was estimated as $w_0 = 2.46 \, \mu m$ by iteratively adjusting $w_0$ and $q$-transforming the beam until a value was found for which the calculated beam divergence matched with that observed from experimental with the bare fiber. Output of the lens-tipped fiber was simulated by beginning with the Gaussian beam of radius $w_0$ at the core and sequentially applying $q$-transformations that account for refraction at the fiber/SU-8 interface, propagation through the SU-8 material, and
refraction at the curved SU-8/air interface, and finally propagation through air to a given distance measured from the fiber tip.

2.4.3. Relating peak photon flux to measured average power

In the next section, an exposure model using the incident peak photon flux was used. The relationship between the measured average power and peak photon flux is derived here. The temporal and spatial distribution of the irradiance at the focal plane is described as:

\[ I(r,t) = I_0 T(t) S(r) \]  \hspace{1cm} (2.13)

\[ T(t) = \exp \left[ -4 \ln 2 \left( \frac{t}{\tau} \right)^2 \right] \]  \hspace{1cm} (2.14)

\[ S(r) = \exp \left[ -\frac{2r^2}{r_0^2} \right], \]  \hspace{1cm} (2.15)

where \( T(t) \) is the normalized temporal profile of a Gaussian pulse, \( S(r) \) is the normalized symmetric spatial profile at the focal plane \((z = 0)\), and \( I_0 \) is the peak irradiance at \( r = 0 \) and \( t = 0 \). The total energy delivered by a pulse \( E_p \) is obtained by integrating Equation. 2.13 with respect to \( t \) and area:

\[ E_p = \iiint_{time\ area} I(r,t)\,dAdt \]  \hspace{1cm} (2.16)

\[ E_p = I_0 \int_{-\infty}^{+\infty} T(t)\,dt \int_{0}^{\infty} 2\pi r S(r)\,dr. \]  \hspace{1cm} (2.17)

The evaluation of both integrals gives:
\[
\int_{-\infty}^{\infty} T(t) dt = \int_{-\infty}^{\infty} \exp \left[ -4 \ln 2 \left( \frac{t}{\tau} \right)^2 \right] dt = \tau \sqrt{\frac{\pi}{4 \ln 2}}
\] (2.18)

\[
\int_{0}^{\infty} 2\pi r S(r) dr = \int_{0}^{\infty} 2\pi r \exp \left( \frac{-2r^2}{r_0^2} \right) dr = \frac{\pi r_0^2}{2}.
\] (2.19)

Substituting 2.18 and 2.19 into 2.17 gives the total pulse energy as:

\[
E_p = I_0 \left( \tau \sqrt{\frac{\pi}{4 \ln 2}} \right) \left( \frac{\pi r_0^2}{2} \right).
\] (2.20)

For multiple pulses delivered at the repetition rate of the laser, the average power delivered per second is just the product of the single-pulse energy times the repetition rate \( f_{\text{rep}} \):

\[
\langle P \rangle = E_p f_{\text{rep}}.
\] (2.21)

Substituting 2.21 into 2.20 and solving for \( I_0 \) gives:

\[
I_0 = \frac{\langle P \rangle}{f_{\text{rep}}} \left( \frac{2}{\pi r_0^2} \right) \left( \frac{1}{\tau} \sqrt{\frac{4 \ln 2}{\pi}} \right) = 0.598 \times \frac{\langle P \rangle}{f_{\text{rep}} \tau r_0^2}.
\] (2.22)

The peak flux is found by dividing the peak irradiance by the energy per photon which gives:

\[
F_0 = 0.598 \times \frac{\langle P \rangle}{f_{\text{rep}} \tau r_0^2 \hbar \omega}.
\] (2.23)

2.4.4. Analytical model of line width scaling

To interpret the measured line width scaling with scan speed \( v \) and average laser power \( \langle P \rangle \), as well as determine the number of photons absorbed in the mpDLW process, an analytical
model was developed and derived. In a similar manner as previous researchers, we start from the
generalized excitation rate equation, given in Section 1.2.2)[37, 48, 58, 92]:

\[
\frac{dN_{ex}}{dt} = \frac{1}{n} \sigma^{(n)} N_g F^n.
\] (2.24)

We assume there is only one dominant process occurring but when non-integer values are measured, that can indicate the presence of mixed absorption process of different \( n \). Due to other competing excited state decay mechanisms, not all of the excited molecules will yield acid. The rate of acid generation as a function of the excitation rate is:

\[
\frac{dN_{acid}}{dt} = \phi_H^+ \frac{dN_{ex}}{dt},
\] (2.25)

where \( N_{acid} \) is the number density of generated Brønsted acid, and \( \phi_H^+ \) is the quantum yield toward acid generation. For these studies, we assume the acid-yield is independent of wavelength. By assuming negligible amount of excited and intermediate species, as well as negligible stimulated de-excitation, the rate of acid generation is:

\[
\frac{dN_{acid}}{dt} = \frac{1}{n} \phi_H^+ \sigma^{(n)} (N_{g0} - N_{acid}) F^n,
\] (2.26)

where \( N_{g0} \) is the initial number density of ground state PAG molecules.

To model the photon flux with respect to time and position within the material, we adopt an exposure model that can be viewed as an array of single-pulse exposures which are spaced along the scan direction \( x \) and perpendicular to the beam axis \( z \). This approach was first suggested by Seet et al. as for overlapping Gaussian pulses [59] and later used also by Shukla et al. for an infinite scan line [48]. An example of overlapping Gaussian profiles is shown in
Figure 2.12 where the parameters used are \( r_0 = 360 \) nm and the pulse-to-pulse pitch spacing \( \Delta = 300 \) nm (thus giving a ratio \( \Delta/r_0 = 1.2 \)). A 3D visualization of the line scan model is shown in Figure 2.13 with all relevant spatial axes shown. The photon flux associated with a single pulse is expanded in terms the peak flux \( F_0 \) and the spatial \((S)\) and temporal \((T)\) distribution:

\[
F = F_0 \cdot S(x, y) \cdot T(t),
\]

where \( x \) and \( y \) are the in-focal-plane distances of the beam from an exposure point located at the origin, and the \( x \)- and \( y \)-axes are parallel and perpendicular to the scan direction, respectively. Assuming a Gaussian temporal pulse shape and perfect Gaussian focusing:

\[
S(x, y) = \exp\left(-\frac{2(x^2 + y^2)}{r_0^2}\right),
\]

\[
T(t) = \exp\left[-4\ln 2 \left(\frac{t}{\tau}\right)^2\right].
\]

Substituting Equations 2.27 - 2.29 into 2.26 gives:

\[
\frac{dN_{\text{acid}}}{dt} = \frac{1}{n} \phi_s \sigma^{(n)} (N_{\text{g,0}} - N_{\text{acid}}) F_0^n \exp\left(-\frac{2(x^2 + y^2)}{r_0^2}\right) \exp\left[-4\ln 2 \left(\frac{t}{\tau}\right)^2\right]^n,
\]

where we note that the flux distribution functions are then each raised by power \( n \). We assume that the beam is effectively stationary during a single pulse, so \( S \) can be taken to be independent of \( t \) and there is no temporal overlap of pulses. Equation 2.27 can then be integrated over time for a single pulse as:
\[
\int_0^{N_{\text{acid}}} \frac{dN_{\text{acid}}}{(N_0 - N_{\text{acid}})} = \frac{1}{n} \phi (n) F_0^n \exp \left( \frac{-2(x^2 + y^2)}{r_0^2} \right) \int_{-\infty}^{+\infty} \exp \left[ -4n \ln 2 \left( \frac{t}{\tau} \right)^2 \right] dt \tag{2.31}
\]

\[
\ln \frac{N_{x0}}{N_0 - N_{\text{acid}}} = \frac{1}{n} \phi (n) F_0^n \exp \left( \frac{-2(x^2 + y^2)}{r_0^2} \right) \sqrt{\frac{\pi}{4n \ln 2}}. \tag{2.32}
\]

Figure 2.12. Overlapping Gaussian irradiance profiles, each representing a single pulse, spaced apart in time (and this x) by \(\Delta\). The spacing of the pulses depends on the scan speed of the stage, \(v\), and laser pulse repetition rate, \(f_{\text{rep}}\). The parameters used are \(r_0 = 360\) nm, \(\Delta = 300\) nm.
Figure 2.13. Perspective view of Gaussian intensity profiles, each representing a single pulse, spaced apart by $\Delta$. For clarity, $\Delta \gg r_0$ so the pulses are not overlapping. The pulses are aligned parallel to the scan direction ($x$-axis) and perpendicular to the $z$-axis (beam axis) and $y$-axis.

The total exposure received by a given point can be thought of as an infinite train of pulses that are partially overlapping and spaced along $x$ by $\Delta = v/f_{\text{rep}}$, where $v$ is the scan speed. Therefore the total exposure at a given point can then be calculated as a summation over all pulses, where each has a normalized irradiance given by $S(x,0)$. The photon flux due to an $i$-th pulse far from the exposure point ($i = -\infty$) is very weak, but it peaks for the 0th pulse that end up centered at the exposure point ($i = 0$), and it again becomes extremely weak again for the $+i$th pulse that strikes the sample at a point well away from the exposure point ($i = +\infty$). Considering
exposure points with coordinates \((x, y)\), the spatial distribution is divided into separate components \(y\) and \(x = i \times \Delta\):

\[
\ln \frac{N_{g0}}{N_{g0} - N_{acid}^f} = \frac{1}{n} \phi_H \sigma^{(n)} F_0^n \exp \left(\frac{-2y^2}{r_0^2}\right) \times \left[ \sum_{\Delta<\infty} \exp \left(\frac{-2(i \Delta)^2}{r_0^2}\right) \right] \sqrt{\frac{\pi}{4 \ln 2}} \quad (2.33)
\]

\[
\Delta = \frac{v}{f_{rep}}. \quad (2.34)
\]

In the case where the pulses are closely spaced such that \(\Delta \ll r_0\), the summation can be estimated as an integral:

\[
\ln \frac{N_{g0}}{N_{g0} - N_{acid}^f} = \frac{1}{n} \phi_H \sigma^{(n)} F_0^n \exp \left(\frac{-2ny^2}{r_0^2}\right) \times \int_{-\infty}^{+\infty} \exp \left(\frac{-2n\Delta^2}{r_0^2} i^2\right) di \sqrt{\frac{\pi}{4 \ln 2}} \quad (2.35)
\]

\[
\ln \frac{N_{g0}}{N_{g0} - N_{acid}^f} = \frac{1}{n} \phi_H \sigma^{(n)} F_0^n \exp \left(\frac{-2y^2}{r_0^2}\right) \left[ \frac{\pi}{2n} \left( \frac{r_0 f_{rep}}{v} \right) \right] \sqrt{\frac{\pi}{4 \ln 2}}. \quad (2.36)
\]

By setting the threshold condition \(N_{acid}^f = N_{acid}^{th}\) in which polymerized SU-8 appears, we solve for the region \(2y\) which is the full-width of the polymerized line:

\[
2y = \sqrt{2r_0} \left[ \ln \left( \frac{F_0}{\frac{K_p}{\sqrt{R_e}}/n} \right) \right]^{1/2} \quad (2.37)
\]

\[
K_p = \ln \frac{N_{g0}}{N_{g0} - N_{acid}^{th}}
\]
If a feature is to be generated \((2y > 0)\), then the argument of the natural logarithm in Eq. 2.37 must exceed unity. Based on this criterion, a threshold photon flux \(F_0^{th}\) can then be defined as:

\[
\begin{align*}
F_0^{th} &= \left( \frac{K_p}{R_a} \right)^{\frac{1}{n}} \\
\langle P \rangle^{th} &= \frac{1}{\gamma} \left( \frac{K_p}{R_a} \right)^{\frac{1}{n}} \\
\gamma &= \frac{2}{\pi r_0^2 f_{rep} (\hbar \omega)}
\end{align*}
\]

where \(F_0^{th}\) and \(<P>^{th}\), are the threshold peak photon flux, and threshold average power, respectively. Equation. 2.39 uses a proportionality constant \(\gamma\) to relate the average power to the peak photon flux, again assuming Gaussian pulses and focusing (see Section 2.4.3). Equation 2.39 is substituted into Equation 2.32 to give a direct relationship between line width and measured average power:

\[
line-width(<P>) = \sqrt{2} r_0 \ln \left( \frac{<P>}{\langle P \rangle^{th}} \right)^{\frac{1}{2}}.
\]

From Equation. 2.39, the value of \(n\) can be determined by varying one of the variables inside the fraction of \(K_p/R_a\) and observing the resulting scaling of \(<P>^{th}\). We take \(\nu\) “out” of \(R_a\) and put Equation. 2.39 into linear form:
\[
\ln \left( \frac{P}{P_{th}} \right) = \frac{1}{n} \ln \nu + \beta
\]  
(2.41)

\[
\beta = \ln \left( \frac{1}{n} \frac{K_p}{\phi_H \sigma^{(n)} (\frac{\pi}{4n \ln 2})^{\frac{1}{2}} (\frac{\pi}{2n})^{\frac{1}{2}} r_0 f_{rep}}{- \ln \gamma} \right)
\]

A plot of \( \ln(<P>_{th}) \) versus \( \ln(\nu) \) gives a line of slope \( 1/n \) and indicated intercept. The value of \(<P>_{th}\) was found by fitting the experimental line width data to Equation 2.40 using \(<P>_{th}\) and \(r_0\) as free parameters.

2.4.5. Numerical simulation of focusing through index mismatched media

To interpret the experimental results from varying writing depth, the IPSF of a high-NA focus was calculated using a vectorial diffraction model that includes spherical aberration from focusing through refractive index mismatched media [93, 94]. Assuming a linearly polarized plane wave of uniform amplitude \((A)\) going through the objective, the electric field \((E)\) and irradiance distribution of the focus inside the SU-8 material is:

\[
E(r, \varphi, z) = -iA \left[ I_1 + \cos(2\varphi)I_3 e_x + \sin(2\varphi)I_5 e_y - 2i \cos(\varphi)I_2 e_z \right],
\]
(2.42)

\[
I(r, \varphi, z) = |E(r, \varphi, z)|^2 = |I_1|^2 + |I_2|^2 + 4|I_3|^2 \cos^2(\varphi) + 2 \text{Re} \{I_1I_3^*\} \cos(2\varphi).
\]
(2.43)

A spherical coordinate system is used here in which, \(r\) and \(z\) are the radial and axial coordinates, respectively. The azimuthal angle, \(\varphi\), is defined with respect to the direction of the incident light.

The integrals \(I_1, I_2,\) and \(I_3\) are:
\[ I_1(r, z) = \int_0^\alpha \sqrt{\cos \theta_1 \sin \theta_1 (T_s + T_p \cos \theta_2)} J_0(k_o r n_1 \sin \theta_1) \exp(i \phi + i k_o z n_2 \cos \theta_2) d \theta_1, \]  
(2.44)

\[ I_2(r, z) = \int_0^\alpha \sqrt{\cos \theta_1 \sin \theta_1 (T_s \sin \theta_2)} J_0(k_o r n_1 \sin \theta_1) \exp(i \phi + i k_o z n_2 \cos \theta_2) d \theta_1, \]  
(2.45)

\[ I_3(r, z) = \int_0^\alpha \sqrt{\cos \theta_1 \sin \theta_1 (T_s - T_p \cos \theta_2)} J_0(k_o r n_1 \sin \theta_1) \exp(i \phi + i k_o z n_2 \cos \theta_2) d \theta_1, \]  
(2.46)

where \( k_0 = 2\pi/\lambda \) is the wavenumber in vacuum, \( \alpha = \sin^{-1}(NA/n_1) \) is the maximum half angle of the cone of light collection, \( \theta_1 \) and \( \theta_2 \) are the angles in which rays propagate in the objective oil and SU-8, respectively, and \( T_s \) and \( T_p \) are the Fresnel transmission coefficients for the s- and p-polarized light, respectively. The spherical aberration caused by index mismatch between oil and SU-8 is represented by \( \phi \):

\[ \phi = -k_0 d \left( n_1 \cos \theta_1 - n_2 \cos \theta_2 \right). \]  
(2.47)

The calculated IPSF is normalized by:

\[ IPSF(r, \varphi, z) = I(r, \varphi, z) / I_0, \]  
(2.48)

where \( I_0 \) is the peak irradiance of the focused beam under no refractive index mismatch. Note that \( I_0 \) is also the peak irradiance when \( d = 0 \) (at the SU-8 surface) because the focus is yet to pass through the SU-8/oil interface and is undistorted. All calculations were done using \( \lambda = 800 \text{ nm}, n_1 = 1.51, n_2 = 1.59 \) and \( NA = 1.4 \).
CHAPTER 3: EFFECT OF PRE- AND POST-EXPOSURE PROCESSING CONDITIONS ON SU-8 MULTI-PHOTON DIRECT LASER WRITING

3.1. Introduction

Table 3.1 is a list of the processing conditions used by various groups for mpDLW in SU-8 (listed in order of decreasing feature size). Each of the conditions used were likely developed based on the desired application, but this only works as a guide to what conditions should be used. While there is general knowledge as to how these conditions affect mpDLW using SU-8, little if any discussion is given as to how or why certain parameters were chosen. In the course of working with SU-8 for the work described in this dissertation, several pre- and post-exposure processing conditions were studied and their effects on mpDLW using SU-8 are reported here.
Table 3.1. Processing conditions of mpDLW of SU-8 used by various groups. MCC = MicroChem Corporation, GBL = gamma butyrolactone, ITX = isopropylthioxanthone, AR = aspect ratio

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Material</th>
<th>Pre-bake</th>
<th>Exposure</th>
<th>PEB</th>
<th>Develop</th>
<th>size</th>
</tr>
</thead>
<tbody>
<tr>
<td>[15]</td>
<td>SU-8 25 25 μm thickness</td>
<td>100 °C 15 min</td>
<td>800 nm 120 fs single shot 60 μJ</td>
<td>100 °C 30 min</td>
<td>MCC developer 30 min</td>
<td>50 μm</td>
</tr>
<tr>
<td>[64, 95]</td>
<td>SU-8 0.975-500 μm thickness</td>
<td>95 °C 10 min -10 hr.</td>
<td>796-800 nm 69 fs 80 MHz 0.25-5.06 nJ (20-405 mW) 10x NA 0.3 2-70 μm s⁻¹</td>
<td>95 °C 15 min</td>
<td>PGMEA IPA rinse N₂ dry</td>
<td>1-6 μm</td>
</tr>
<tr>
<td>[22]</td>
<td>SU-8 2035 50 μm thick ITX added</td>
<td>95 °C 30 min</td>
<td>800 nm 120 fs 76 MHz 1-10 mW 60x NA 1.4 50 μm s⁻¹</td>
<td>95 °C 15 min</td>
<td>PGMEA IPA rinse 150 °C 15 min</td>
<td>600 nm AR 3</td>
</tr>
<tr>
<td>[20, 21, 96]</td>
<td>SU-8 65 °C</td>
<td>800 nm 120 fs 100x NA 1.4</td>
<td>65 °C-95 °C 6 min</td>
<td>GBL 1 hr.</td>
<td>150 nm AR 2.7</td>
<td></td>
</tr>
<tr>
<td>[58]</td>
<td>SU-8 20 μm thick</td>
<td>95 °C 4 min</td>
<td>800 nm 130 fs NA 1.4 0.3 nJ 10 μm s⁻¹</td>
<td>95 °C 5 min</td>
<td>MCC developer 4 min</td>
<td>50 nm</td>
</tr>
</tbody>
</table>

3.2. Pre-exposure bake

The purpose of baking the film before exposure is to remove solvent (cyclopentanone and in a certain extent propylene carbonate) that remains after spin coating. Solvent remaining in the resin significantly decreases film viscosity which increases the diffusion length of Brøsted acid during the post-exposure bake, and lowers solubility contrast [97]. In some cases, solvent
content can vary with film depth, due to the film surface becoming more viscous at a faster rate and hindering further evaporation of solvent below the surface [52, 98, 99]. The bake-time required typically depends on the film thickness, ranging from 15 minutes for a 50 µm film to 10 hours for a 500 µm film [15, 22, 64]. Higher temperature increases the rate of solvent evaporation, but high temperatures are avoided because the PAGs can be thermally activated around 130 °C [100, 101].

In Figure 3.1 are perspective SEM images of a large area photonic crystal fabricated on a SU-8 film pre-exposure baked for ~2 hours. One observed effect is the partial delamination of the crystal from the substrate which appears to be due to shrinkage of the material. Previous researchers have found that SU-8 shrinkage can occur during the development process due to poor cross-link density [53]. Another observed effect is the presence of overlapping line features near the top of the structure. This type of distortion can occur when there is more solvent remaining in those regions, allowing the generated photoacid to diffuse out faster [97, 102]. A simple description of these phenomena is shown in Figure 3.2. When the solvent content is low the photoacid remains confined near their point of generation, and the resulting cross-link density is high, but under higher solvent content, the photoacid will diffuse further out, not only giving a larger feature, but a feature with less cross-link density that is susceptible to various modes of distortion such as development shrinkage. Another description of diffusion during mpDLW was given by Misawa et al., but it should be noted that the active species is diffusing in liquid resist during the exposure process, so the diffusion occurring here is affected by a different string of processes [103]. Regardless, these preliminary results would imply that insufficient pre-exposure bake can give distorted structures fabricated by mpDLW.
Figure 3.1. Perspective SEM images of a 100 x 100 μm photonic crystal fabricated on a SU-8 film pre-exposure baked for ~2 hours.

Figure 3.2. Illustration of photoacid diffusion. (Left) Acid is generated but remains well confined in the region they were created. (Right). The same amount of acid is generated but diffuses farther away from their origin creating a larger feature with less cross-link density.
Following this hypothesis, a simple experiment was performed to understand how SU-8 features were affected the pre-exposure bake duration and solvent content. Figure 3.3 is a plot of the solvent remaining in the SU-8 film as a function of pre-exposure bake duration. The solvent content was determined by $^1$H-NMR spectroscopy. Despite a two hour bake (which is ~10 times more than the recommended by the commercial supplier), there is still a significant amount of solvent remaining in the film. Only after a 16-hour bake was the solvent content was observed to fall below ~1 wt-%.

![Figure 3.3. Plot of solvent content of a ~40-μm-thick SU-8 film as a function of pre-exposure bake duration.](image)

To assess the effect of the remaining solvent content. Photonic crystal (PhC) [22, 104] structures were fabricated from SU-8 films that were pre-baked for 0.5, 2, and 12 hours. The photonic crystal design is face-centered-tetragonal (FCT) “stack-of-logs”. In this configuration, parallel logs are spaced apart by $a$ in the first layer. On the second layer, the logs have the same spacing but are oriented perpendicularly to
the first. On the third layer, the logs are oriented in parallel with the first layer, but laterally offset by $a/2$. Logs in the fourth layer are in parallel with the second, and are laterally offset by $a/2$. Each layer is vertically spaced by $c/4$. Repeating these four basis layers gives the FCT PhC. Due to the large area of the PhC, a support wall is included minimize distortion. SEM images of the structures are shown in Figure 3.3. In the 0.5-hour structure, almost nothing remains of the stack-of-logs structure; only the support walls remain. This is attributed to the high solvent of the film promoting rapid acid diffusion, resulting in features with low cross-link density that do not survive the developing. The corners of the support walls also appear very rounded, which is another indication of diffusion. On the two-hour structure, it can be seen that the lines have survived developing, but have been merged together. The 12-hour structure appears to give the best fidelity, which appears to suggest that longer pre-exposure bake duration and less solvent content could yield better fidelity structures. Seet et al. reached a similar conclusion, although they did not report what bake-time was needed to achieve the best results [24]. Work by our group has shown that removing as much solvent as possible via vacuum evaporation yielded the most robust structures [61]. Following this, a pre-exposure bake-time of 14 hours was adopted.
Figure 3.4. SEM images of micro-structures created using different pre-exposure bake duration.

3.3. Laser parameters

Figure 3.5 is a plot of the temporal profile of the laser pulses produced by the continuous-wave mode-locked Ti:sapphire laser used for the majority of work as measured with the GRENOUILLE pulse measurement device and calculated using the FROG method [105]. The data were both fit to a Gaussian and a sech$^2$ temporal profile, giving $R^2$ values of 0.999 and 0.995, respectively. On the basis of the fit, it can be concluded that the temporal profile of the laser pulses is best described as Gaussian.
Figure 3.5. FROG trace of pulses generated by the continuous-wave mode-locked Ti:sapphire laser used for the majority of work in this dissertation. Two best fits are shown for the Gaussian and Sech² pulse profiles. It can be concluded here that the pulses are Gaussian shaped.

3.4. Developing of patterned SU-8 film

After exposing an SU-8 film, the unexposed portion is dissolved away by immersing the film in a solvent. The time required to dissolve all of the unexposed material generally depends on the thickness, but there can be other factors. Complex structures, such as those having deep trenches or porous networks, require more time to develop fully. This is because the solvent and dissolved SU-8 must travel at longer distances through small micro-channels in the structure to clear through. The effect of the development step on the fidelity of an SU-8 structure depends on
the internal cross-link density. Structures with low-cross-link density will undergo development shrinkage, where the remaining oligomers are easily leached out of the feature by the solvent [53]. On the other hand, highly cross-linked features can resist the solvent and remain intact for extended development times [106]. If the structure is well cross-linked, the only risk to long development time is that the polymer may swell enough to the point that it delaminates from the substrate [52]. We observe that long development time does not noticeably affect the structures. The development time used in these studies is as long as needed to dissolve all of the unexposed material from both the structure and underlying substrate, which is typically 10 to 20 minutes for a ~40 μm film.

After developing the structure, the solvent is removed, rinsed, and dried. The structures fabricated in these studies consist of closely spaced walls. As the solvent dries away from the walls, it pulls the walls together due to surface tension, and in some cases the walls delaminate and collapse toward each other [107, 108]. A common result of this occurrence is shown in Figure 3.6, where one of the walls delaminated and is tilted toward the other walls. Close observation (see Figure 3.7) of these walls during post-processing show that the walls did indeed delaminate during the drying step.
Figure 3.6. Side view SEM image of lines suspended by walls. The left-most wall has delaminated from the substrate and is tilted toward the second wall.
Figure 3.7. Optical top view images of the wall structure shown in Figure 3.8 at various stages during the development process: (Top) immediately after post-exposure bake, (Middle) after developing, and (Bottom) after drying. The distortion and tilting of the left-most wall evidently occurred during the drying process.

The distorting effect of surface tension can be somewhat controlled by progressively diluting the developer through solvents that have adhesion to SU-8, ending with water before allowing the structure to dry [107]; however, a simpler method used for these studies was to increase the power used to fabricate supporting walls. Exposing with a higher power increased
the amount of photoacid generated which increased the overall cross-link density of walls, especially at the substrate/SU-8 interface. This hypothesis was tested by fabricating free standing walls without suspended lines with increasing power. The result can be seen in Figure 3.9, where again the walls remained intact during the development process, but collapsed during the drying step. Collapse and distortion does not occur when $<P> = 3.0$ mW, which appears to support the hypothesis. Interestingly, cleaning the substrate by immersing in 1 M KOH (aq) solution appears to slightly improve the fidelity of the walls. The walls made with 2.5 mW do not collapse, and there is noticeably fewer walls collapsed at $<P> = 2.0$ mW. One reason for this result may be that the KOH treatment changes the surface energy of the glass and enables SU-8 to better adhere to it.

![Figure 3.9](image).

**Figure 3.9.** Effect of exposure power and substrate preparation on the overall fidelity of microfabricated walls. Lower exposure power tends to result in walls collapsing together. KOH cleaning of the underlying substrate appears to decrease the exposure power needed to prevent delamination.
CHAPTER 4: EFFECT OF REFRACTIVE INDEX MISMATCH ON MULTI-PHOTON DIRECT LASER WRITING

Work in this chapter was published as

Henry E. Williams, Zhenyue Luo, and Stephen M. Kuebler,


4.1. Introduction

It has been reported that DLW is affected by refractive index contrast (RIC, see Figure 4.1) between the high-NA focusing objective (or objective immersion oil, \( n_1 \)) and the writing material (\( n_2 \)) because the refractive index mismatch introduces spherical aberration that distorts the focused irradiance point spread function (IPSF) and consequently changes the size and shape of photo-patterned features [25, 109, 110]. For example, Wegener et al. investigated the effect of RIC when performing mpDLW in As\(_2\)S\(_3\) chalcogenide glasses (\( n_2 = 2.5 \)) and found that the aspect ratio (height/width) of the written features changes greatly with focal depth [110]. Gu et al. studied laser patterning in lithium niobate (LiNbO\(_3\), \( n_2 = 2.2 \)) and concluded that RIC causes the written voids to become larger and more distorted with increasing focal depth [25]. The effect of RIC on DLW in silica has also been examined [111], and it was found that secondary maxima in the IPSF can substantially elongate the photo-damaged regions [109]. To date, most research has focused on large RIC. Although a few reports discuss how low RIC affects laser induced damage [109, 112], these results cannot be readily applied to mpDLW because it proceeds via a different mechanism.
Figure 4.1. Schematic of the focusing geometry used to study the effect of RIC on multi-photon direct laser writing (mpDLW). A linearly polarized plane wave is focused by a high numerical aperture oil-immersion objective lens into a film of SU-8 resin, where an RIC of \( n_2 - n_1 = +0.08 \) exists between the oil and the resin. The expected focal distance is \( d \), and the focal shift resulting from RIC is \( \Delta f \), so the actual focal distance is \( d + \Delta f \). Note that not all features in this illustration are shown to scale.

Several approaches have been proposed to compensate for spherical aberration due to RIC encountered in confocal microscopy, optical trapping, and DLW. Luo et al. compensated for RIC by adjusting the refractive index of the immersion oil [39]. This method must be optimized for a single focal depth or to achieve a good compromise in performance over all focal depths used, but it cannot in general eliminate the effects of RIC at all patterning depths. Another approach is to alter the tube length of the objective [113]. However, this method does not provide dynamic compensation when writing at different depths. A more elaborate approach
uses adaptive optics and an active feedback-loop to correct dynamically for spherical aberration at different depths [114]. Beam-shaping elements have been developed that cause the focal spot to vary slowly with spherical aberration [115].

A common implementation of mpDLW involves focusing the laser beam through a coverslip, which can support the photoactive medium above. Yet, the high numerical aperture (NA) objectives typically used have a short working distance of \textit{circa} 200 \( \mu \text{m} \) or less, so including the cover slip greatly reduces the maximum focusing depth and therefore height of microstructures that can be created. Additionally, mpDLW is promoted as a technique for integrating micro-devices directly onto arbitrary surfaces, including opaque, curved, or micro-patterned substrates bearing devices created by other means. Examples include several demonstrations of mpDLW onto silicon substrates [35, 116, 117].

Here we report the effect of refractive index mismatch on mpDLW in the case of small RIC. We consider the situation in which the laser light is focused directly into the photopolymer, without traversing through a coverslip, as in Figure 4.1. SU-8 has a value of \( n_2 = 1.59 \) at 800 nm, which is quite close to that of the immersion oil \( (n_1 = 1.51) \) used with the high-NA objective. Suspended-line microstructures were fabricated by mpDLW in films of SU-8 and the dimensions of the resulting lines were characterized as a function of the average focused laser power \( \langle P \rangle \). Even for such small RIC, the experimental data show that the fabricated line-height can vary by as much as 40\%, so the effect of spherical aberration on mpDLW is significant even for small RIC of \( n_2 - n_1 = +0.08 \). A vectorial diffraction model is applied to calculate the IPSF and to interpret the observations [93, 94]. In particular, we studied how feature-size changes versus depth as a function of \( \langle P \rangle \). From the experimental data and simulation results, we identify the
influence of spherical aberration on the feature size and shape under the condition of small RIC. Finally, we show that feature-size variation throughout the depth can be minimized by choosing an optimum laser power or modulating the laser power as a function of focal depth. This approach does not eliminate RIC but rather compensates for its effect on feature size in a way that is simple to implement.

4.2. Varying writing depth

Following Figure 4.1, the focal spot could be buried into the resin to an expected focal depth, \( d \), by translating the sample toward the objective by the same amount. RIC between the immersion oil and SU-8 distorts the IPSF and displaces the actual focus by \( \Delta f \). Translating the sample from the SU-8/oil to the SU-8/glass interfaces gave a value for the apparent thickness of the resin. Note that because the apparent thickness is measured optically, RIC causes it to differ from the actual thickness of the resin film.

Given the \( NA \) of the objective the beam diameter is estimated to be 170 \( \mu m \) or less at the oil/resin interface when the beam is focused to a depth of 35 \( \mu m \). Stylus profile scans show that the film surface is flat to within 40 nm (\( \lambda/20 \)) over 170 \( \mu m \), and it slopes linearly with no appreciable curvature. This implies that the resin interface itself introduces negligible spherical aberration.

The suspended-line microstructures were characterized by SEM (Figure 4.2). The wall height observed by SEM is used to measure film thickness and provides a reference point for the SU-8/oil interface (the film surface), and the distance from this point to the substrate represents the true thickness of the resin film. The true resin depth of the lines, \( d + \Delta f \), was measured as the
distance between the line and the SU-8/oil reference (see Figure 4.2c). Each of the lines between a certain pair of walls was fabricated under the same average power, $<P>$. which allows to observe how the line size scales with writing depth. Conversely, all of the lines that were fabricated in the same writing depth were compared to observe how line size scales with $<P>$ at a given writing depth.

**Figure 4.2.** (a) Top-view and (b) side-view images of a suspended-line microstructure obtained by scanning electron microscopy. (c) Side-views of the suspended lines.
4.3. Discussion

The measured variation of line-width and height as a function of actual writing depth is shown in Figure 4.3. For any given writing depth, both line-width and line-height increase with \( <P> \); however, the rate of increase is neither constant, and in some cases, it decreases. Additionally, the line-height appears to be more sensitive to changes in \( <P> \) and focal depth than line-width. The variation in line-width and height versus \( <P> \) is more significant at greater focal depth, particularly for depths greater than 25 \( \mu \text{m} \). At low powers, the line-height and line-width decrease with writing depth. At \( <P> = 1.53 \text{ mW} \), the line height decreases by 40\% when the writing depth is increased from 4.9 \( \mu \text{m} \) to 35.3 \( \mu \text{m} \). Typically in mpDLW, the exposure power used is above the threshold where a polymerized line can appear, but as low as possible in order to create the smallest features. Figure 4.3 shows that despite the small RIC, the size of the lines are greatly affected by writing depth at low powers, which means that in order to write tall (at least around 40 \( \mu \text{m} \)) structures with small and stable feature size, the RIC effect must be taken into account. At high \( <P> \), the line height increases with writing depth. At \( <P> = 3.77 \text{ mW} \) the line height increases by 9\% when the writing depth is increased from 4.9 \( \mu \text{m} \) to 16.1 \( \mu \text{m} \). At intermediate power, the overall trend in line width is less dramatic; however, the line height initially increases with writing depth and then decreases again.
Figure 4.3. (a) Width and (b) height of suspended lines created by mpDLW in SU-8 as a function of the average focused power \(<P>\) and actual focal depth \((d + \Delta f)\). These data were obtained from SEM images of suspended-line microstructures like that in Figure 4.2.
Compared to the ascending scan method [118], the suspended-line approach used here offers two advantages for investigating the dimensions of written features. First, in the ascending-scan method it is difficult to observe small features, with width on the order of 200 nm or below, as these are least likely to remain after post-exposure processing. Suspended line features of this size are more readily observed because they are anchored to robust walls. Second, in order to explore the effect of RIC, it is necessary to explore how feature-size changes versus writing depth within the medium. This can be accomplished by ascending-scan method, however films of various thicknesses would have to be prepared, corresponding to writing depth, for each scan. Clearly, this approach is more labor intensive and to the best of our knowledge, this approach has not been attempted.

In Figure 4.4 are plots of the predicted IPSF (axial and radial), beam size (FWHM, axial and radial), focal shift, and peak intensity, which all change with expected depth, \( d \). The axial IPSF (Figure 4.4a) undergoes four distinct changes with \( d \): (1) it becomes asymmetric, (2) the main lobe broadens out, (3) the peak irradiance lowers and experiences focal shift \((+z)\), and (4) the other lobes at \(+z\) increase. These changes are due to spherical aberration when \( n_2 > n_1 \) [93, 94]. The calculated focal shift of the main lobe, \(+z\), as a function of \( d \) is plotted in Figure 4.4c, which is compared to the experimentally measured focal shift, \( \Delta f \) (green squares). Both predicted and measured focal shifts agree well with each other within error, following a semi-linear increase with increasing \( d \). This trend was predicted with a simpler ray tracing model [112]. In Figure 4.4b is a plot of the transverse IPSF. The transverse IPSF depends on the \( z \) chosen, so the IPSFs shown for each \( d \) are at values of \( z \) where their main lobes are at their highest peak irradiance. From the plots, it is clear that the peak decreases with \( d \), but the
transverse FWHM changes slightly. Figure 4.4d and Figure 4.4e show the axial and transverse FWHM of the main lobe. When $d$ is increased from 0 to 30 $\mu$m, the axial FWHM increases by 60%, but the transverse FWHM increases by only 15%. Finally, Figure 4.4f shows the peak irradiance is 40% of $I_0$ when $d = 30 \mu$m.

**Figure 4.4.** Numerical simulations of the IPSF versus *expected* focal depth $d$ when $n_1 = 1.51$ and $n_2 = 1.59$. (a) Axial and (b) transverse IPSF for three depths. (b) Simulated values (*blue trace*) and experimental values (*green-filled squares*) of the focal shift $\Delta f$ versus $d$. (d) Axial FWHM, (e) transverse FWHM, and (f) normalized peak irradiance versus $d$. 
To interpret the experimental results, we examine how the feature size is predicted to change with focal depth using the simulated IPSFs. An irradiance threshold condition is invoked such that where all points in the SU-8 where the local irradiance $I(r, \varphi, z)$ exceeds a polymerization threshold $I_{th}$, the photo-activated chemistry proceeds sufficiently to form a cross-linked volume that survives the solvent development step and remains intact. This approach neglects the effects of chemical diffusion and shrinkage. Under these assumptions, the suspended lines have width and height that can be estimated from the boundaries of the region around the focal spot that satisfies the criterion:

$$I_0 \times IPSF(r, \varphi, z) > I_{th}, \quad (4.1)$$

$$IPSF(r, \varphi, z) > \frac{I_{th}}{I_0}. \quad (4.2)$$

$I_{th}$ is the threshold irradiance determined by the material properties and the processing conditions. $I_0$ is proportional to $\langle P \rangle$, whereas $I_{th}$ is constant, so the ratio $I_{th}/I_0$ decreases with increasing laser power. On the other hand, it increases with decreasing $\langle P \rangle$ and if $I_{th}/I_0 > 1$ then no features will survive developing at any depth. Where the IPSF is calculated, the width and height of the line features are determined by the regions where $IPSF > I_{th}/I_0$.

The size of the axial IPSF that exceeds the threshold is calculated and plotted in Figure 4.5 for three ratios of $I_{th}/I_0$. From Figure 4.4a, we see the change in peak irradiance and line broadening with increasing focal depth have opposite effects on the size of polymerized features. The drop in peak irradiance tends to decrease the line-height, whereas broadening in the central lobe tends to increase the line-height. The relative influence of these two effects changes with laser power. At low laser power, where $I_{th}/I_0 = 0.4$, the drop in peak irradiance dominates, with
the result that overall the line-height decreases with focal depth. At high laser power, such that \( \frac{I_{th}}{I_0} = 0.2 \), broadening of the central lobe dominates, and the line-height increases with focal depth. At intermediate laser power, \( \frac{I_{th}}{I_0} \approx 0.3 \), the two effects counterbalance each other, so the line-height remains roughly constant with focal depth. These trends are consistent with the experimentally observed variation in line-height discussed above and shown in Figure 4.3.

![Figure 4.5. Size of region of axial IPSF that is above \( I_{th} \) as a function of depth.](image)

The effect of refractive index mismatch on multi-photon DLW is quite different from that reported for DLW in glasses [109, 112]. In this case, the laser power is well above the damage threshold of the material, typically by a factor of ten or more. As a result, axial broadening of the IPSF with focal depth dominates, whereas the decrease in peak-irradiance is less significant, so overall features created by photo-damage simply lengthen with focal depth. Additionally,
when $<P>$ is high enough, even axial or transverse side lobes in the IPSF can exceed the damage threshold contributing to the elongation and distortion of the written features [112]. In contrast, $<P>$ is chosen in mpDLW to be between the polymerization threshold and damage threshold, so side lobes are typically well below the threshold. Even in extreme situations where a side lobe exceeds the threshold, the cross-link density in these regions is likely too weak to survive development. Overall, when mpDLW is performed in a medium with small RIC, both the decrease in peak irradiance and the broadening of the IPSF with focal depth affect the feature size because $<P>$ is specifically set near the polymerization threshold in this technique.

Near the SU-8/oil interface, the line-width and height increase with laser power at roughly the same rate, with both nearly doubling from $<P> = 1.53$ mW to 4.74 mW. As a result, the aspect ratio varies between extremes of 2.48 and 2.63, which is essentially constant within the experimental uncertainty for this ratio ($\pm 0.14$). In contrast, at $d = 35 \mu m$, the line-height nearly quadruples over the range of powers explored, whereas the line-height increases by just under a factor of three. So at this depth, the aspect ratio changes with power by an experimentally significant amount, increasing from 2.37 (at 1.53 mW) to 2.92 (at 4.74 mW). It is also instructive to consider how the aspect ratio varies with focal depth at fixed laser power, as this is the more common experimental situation. At the lowest power used, the aspect ratio is 2.50 near the SU-8/oil interface, decreasing negligibly to 2.37 at $d = 35 \mu m$. The situation is quite different at the highest power used. The aspect ratio is 2.49 near the SU-8/oil interface, but it increases to 2.92 when the focal depth is increased to 35 $\mu m$. So overall we find that both line-height and width can vary with focal power and depth, and when they vary at different rates, this can also change the aspect ratio, depending upon the power and variation in focal depth.
In many cases it is desirable to fabricate 3D structures using conditions that give the same feature size at any depth. 3D photonic crystals exhibit better band-gap properties if they are fabricated with constant feature size because it is simpler to achieve uniform fill factor throughout the lattice [110]. A variation in feature size compromises elasticity and performance of vertical nano-wire structures [34].

The simplest way to obtain uniform feature size versus depth is to choose an average incident laser power $\langle P \rangle$ at which the drop in peak irradiance is nearly offset by the broadening of the IPSF. For the experimental conditions described here, Figure 4.3 shows that $\langle P \rangle = 2.38 - 3.00$ mW yields features that are nearly uniform in size with focal depth. However, this approach is limited to one feature size, a height of $\sim 1.5 \mu m$, is quite noticeably larger than the resolution limit of the process. A more dynamic method involves control of the laser power with focal depth which can be used to improve the uniformity of the line size without sacrificing resolution. First, measurements of line-height (and width) obtained as a function of $\langle P \rangle$ at a given focal depth $d$ were fit to an analytic function[37, 48] that was developed for estimating the size of features generated by mpDLW using a Gaussian beam. Although these equations do not by themselves account for the effect of RIC, the line width and line height data were fit for a particular $d$. By repeating this fitting process for each $d$, an empirical and quantitative description for how feature size changes with $\langle P \rangle$ and $d$ can be made despite the presence of RIC. Next, a targeted feature size is selected and substituted into each equation to find the value of $\langle P \rangle$ that yields the targeted features size as a function of $d$.

To illustrate the approach, we produced two suspended-line structures – one generated at constant $\langle P \rangle = 1.54$ mW, and another for which $\langle P \rangle$ was adjusted with focal depth to maintain
a constant line-height – and we compared the resulting line-heights and widths as shown in Figure 4.6. With constant $<P>$, the line-height is initially 0.95 μm, but it varies with focal depth, increasing up to 0.99 μm and dropping as low as 0.64 μm. Using the procedure described above, we found that $<P>$ should be varied with $d$ as per the inset in Figure 4.6 to maintain a line-height of 0.95 μm at all focal depths. From the suspended-line structure generated using modulated $<P>$, we found that the line-height varies only between 0.90 μm and 1.0 μm, and the variation in line-width is smaller as well. Thus, this simple approach provides a means to achieve more uniform feature size in the presence RIC without the need for additional optical elements or active-control devices, and the method is cost effective and simple to implement.

![Figure 4.6](image)

**Figure 4.6.** Measurements of (left) suspended-line width and (right) height as a function of focal depth. Red squares indicate the dimensions of lines fabricated at a constant laser power of 1.54 mW. The black circles represent the dimensions of lines fabricated when the laser power was adjusted as a function of focal depth, as per the inset.
4.4. Conclusion

This work shows that even a small refractive index mismatch of $\Delta n = +0.08$ can cause a significant variation in the size of features generated by mpDLW using a photo-polymerizable resin. In particular, when the average incident laser power is low and close to the polymerization threshold, the feature height can decrease by as much as 40%. This phenomenon is distinct from the effect of RIC observed in fabrication based on laser-induced damage because the influence of axial side lobes is typically negligible in mpDLW. Additionally, in mpDLW the effects of axial focal spot broadening and decreased peak irradiance oppose one another, such that under low power the feature size tends to decrease with focal depth, whereas at high laser power the feature size actually increases. A vectorial diffraction model was used to interpret these results. It was shown that these observations could be understood by considering how RIC-induced spherical aberration causes the IPSF to change with focal depth relative to a fixed material-dependent polymerization threshold. Last, we have described and demonstrated a simple approach for controlling the variation in feature size that involves modulating the average focused laser power as a function of focal depth.
CHAPTER 5: ORDER OF THE NONLINEARITY OF THE CROSS-
LINKABLE PHOTORESIST SU-8 UNDER MULTI-PHOTON
EXCITATION AND DIRECT LASER WRITING

Work in this chapter is being prepared for publication as

Henry E. Williams, Carlos Diaz, Gabriel Padilla, Florencio E. Hernandez
and Stephen M. Kuebler,

"Order of the nonlinearity of the cross-linkable photoresist SU-8 under
multi-photon excitation and direct laser writing."

5.1. Introduction

The key to determining the order of the nonlinear absorption \( n \) involved during mpDLW for a given material is to understanding how the overall process can be modeled and controlled. Although SU-8 had been widely used for mpDLW, its value of \( n \) remained undetermined. Yet the photo-chemistry was generally assumed to be activated by 2PA at or near \( \lambda = 800 \text{ nm} \), which corresponds to \( n = 2 \). In 2006, Juodkazis et al. reported \( n = 4 \) for mpDLW in SU-8 at \( \lambda = 800 \text{ nm} \) using 180-fs pulses from a 1-kHz repetition rate amplified femtosecond laser and focused average power \( \langle P \rangle \) that corresponded to peak irradiances at or near 2 TW/cm\(^2\). This value was based on measurements of how the feature widths changed as a function of average focused power delivered to the sample \( \langle P \rangle \) and the laser-scan speed \( v \). This apparently high-order nonlinearity was ascribed to avalanche absorption, a fourth order non-resonant process [59]. The order or nonlinear absorption has been measured for other materials. Perry et al. found \( n = 3 \) for DABSB photoinitiator in SR9008/SR368, at \( \lambda = 730 \text{ nm} \), which was assigned to a "2 + 1" multi-photon absorption process [119]. Thiel et al. ruled out \( n = 1 \) and
roughly estimated $n = 2$ for SU-8 (MicroChem) and IP-L (Nanoscribe) photoresists at 532 nm [16]. To the best of our knowledge, the accounts mentioned here are the only reports of finding $n$ directly from a mpDLW process. Z-scan or other spectroscopic methods can be used to find $n$ under more controlled conditions; however, there is great value to having a complementary means for measuring the parameter under conditions which are closest to those actually used for mpDLW.

In this chapter results are presented that provide new insight into the mechanism of nonlinear absorption that drives the photo-chemistry associated with mpDLW in SU-8. An analytical model is presented in chapter 2 that can be used to obtain $n$ for a pre-polymer based on how free-standing single lines created by mpDLW change in width versus $<P>$ and $v$. This model is applied to analyze feature-width data for sets of suspended lines written at various $<P>$ and $v$ over a wavelength range of 725 - 875 nm. The resulting "action spectrum" in $n$ implies that 2PA dominates at short wavelengths, whereas 3PA dominates at 800 nm and longer wavelengths, and a mix of both processes occurs at wavelengths in between. These conclusions are supported by supplemental Z-scan measurements and multi-photon absorption calculations (including 3PA) of the PAG alone.

5.2. Methods

Suspended single-exposure lines were fabricated across 5-μm gaps between supporting walls by mpDLW in 40-μm thick film of commercial SU-8 (Figure 5.2). The walls were left hollow to minimize the total fabrication time. The gap-width was kept small to minimize stresses on the lines, but made no smaller than 5-μm to avoid high surface tension forces that
could collapse the supporting walls. The line features are horizontally spaced by 2.5 μm and are all written no more than ~10 μm from the SU-8/immersion-oil interface, to minimize feature-size distortions that result from refractive index mismatch. Each gap between the walls corresponds to a particular scan speed, starting at 6.25 μm.s⁻¹ and doubling with each set, up to 800 μm.s⁻¹. The actual scan speeds were measured by monitoring the nanopositioner sensors output versus time with an oscilloscope (see Section 2.1.2) and found to match the commanded speed to within ±5%. At higher scan speeds, the finite acceleration of the stage causes the speed to be slower at the start of the line segment. The overall length of each line segment was made sufficiently long so that the stage had reached the commanded speed by the time the beam was traversing the gap between the walls, where the line-width measurement was made. The average power used in these experiments ranged from \( <P> = 0.1 - 6.5 \) mW. The determination of \( <P> \) as a function of scan speed and the corresponding value of \( n \) has been described in Section 2.4.4

5.3. Results and discussion

5.3.1. Comparison of analytical model and numerical simulation of vectorial diffraction

The analytical model derived to interpret line width scaling (Section 2.4.4) assumes the transverse irradiance profile can be well described by a Gaussian function. To assess this claim, a plot of two transverse irradiance profiles at their respective focal planes (where \( I(0,z) \) is the highest) was made. The first profile was calculated for a Gaussian beam with beam waist \( r_0 = 360 \) nm (see Equation 2.15), while the second profile was generated from a numerical simulation of the beam focusing into SU-8 at a focal depth of 30 μm, 800 nm light, and indices of refraction \( n_1 = 1.51 \) and \( n_2 = 1.59 \) (see Section 2.4.5 and Figure 4.4). The two profiles are plotted together.
in Figure 5.1. The simulated profile contains fringes near the wings of the main lobe, while the Guassian profile does not. This is the most apparent difference between the two profiles; however the wings do not increase more than 5% of the main lobe, so these wings will only affect the line width under very high ratios of $<P>/<P>_\text{th}$. The main lobe of the Gaussian and simulated profiles are extremely similar to each other, which means the main lobe can be well described by a Gaussian function up to focal depths of 30 μm (for our experiments the focal depth is typically 10 μm).

![Figure 5.1](image_url)

**Figure 5.1.** Comparison of transverse irradiance distributions at the focal plane for Gaussian focusing (black line, $r_0 = 360$ nm) and numerical simulation of focusing into SU-8 with 800 nm light at a focal depth of 30 μm (red line, $n_1 = 1.51$ and $n_2 = 1.59$, see Figure 4.4).
5.3.2. *Effect of scan speed, average power, and wavelength*

Figure 5.2 shows top views of suspended line features, imaged by SEM. A magnified image of the line features is provided in Figure 5.3. The range of incident powers used to fabricate the lines and walls are particularly important in the determination of $n$. For walls, the power is optimized such that the structure has good adhesion and fidelity, while not being too “overexposed” such that photoacid diffuses over to the line feature which can result in tapering [58]. A closer view of a typical line shown in Figure 5.4 shows negligible tapering. For lines, the minimum power is chosen such that the smallest lines can be developed without too much distortion. The maximum power (or the largest lines used for fitting) is chosen such that other effects such photoacid diffusion, higher order non-linear effects, or even photodamage can be avoided. Lines wider than 700 nm tend to deviate significantly from the analytic model used to extract a value for $n$. This can be due to significant acid diffusion in which a steep gradient of acid concentration is generated from a higher exposures which can result in higher diffusion lengths [97, 120]. Avalanche absorption can begin to become significant at higher irradiances near dielectric breakdown, which will cause a change in line-width scaling [69]. Another possible cause is the presence of non-Gaussian features in the focused IPSF, such as side lobes, which would become significant when $<P>$ is much greater than $<P>_\text{th}$ [121].
Figure 5.2. Top view SEM of suspended line features.

Figure 5.3. 4 kX magnified top view SEM image of suspended lines exposed at 6.25 μm s\(^{-1}\) (center column) and 12.5 μm s\(^{-1}\) (left column).
5.3.3. Determination of threshold average power and order of the nonlinear absorption using continuous-wave mode-locked femtosecond pulses.

Figure 5.5 is a plot of the line width versus average power. Figure 5.6 is a plot of \( \ln(<P>_{th}) \) versus \( \ln(v) \). Using the plot as an example, the values of \( <P>_{th} \) was determined by fitting of the line width versus power for each scan speed (the fit is represented as red lines). Because the curvature of the plot is greatest near the threshold, the value of \( <P>_{th} \) is very sensitive to fluctuations in the line widths from higher powers. Several techniques are employed to improve the uncertainty. First, the line widths are fabricated with a close to the threshold as possible.
without resulting in significant distortion or line breaking. Second, some additional lines are fabricated at moderate levels above the threshold so the full curvature of the line width scaling with power can be seen. Third, a weighted fit using the standard deviation of the individual line widths as weights was employed to minimize the effect of possible outliers on $<P>_{th}$. And finally, the standard error of the fitted parameter served as an overall uncertainty. Typically the standard error of $<P>_{th}$ is within $\pm 1\%$, which means that $<P>_{th}$ can be reasonably attained with acceptable uncertainty.

The value of $r_0$ was also a fitted parameter from the line width data. Because all of the lines are written at the same depth in the material, it stands to reason that $r_0$ should be a shared parameter among the individual scan speeds. Typically the fitted value of $r_0$ varies from $\pm 50$ nm within an experiment. The values of $r_0$ have varied from 350 to 450 nm for all line scans which roughly agree with the diffraction limited estimate of 348 nm for 1.4 NA and 800 nm light. Sources of variation of $r_0$ can include varied index mismatch and spherical aberration due to films with slightly varied index, varied dispersion of the material, varied surface roughness of the film, and variation in the laser alignment.
Figure 5.5. Plot of line width versus average power at various scan speeds at 800 nm

Figure 5.6. Plot of $\ln(<P_{th}>)$ versus $\ln(v)$ at 800 nm. The slope corresponds to $n = 2.9 \pm 0.02$
Table 5.1 is a list of the values of $n$ determined by suspended line scan fabrication at wavelengths 725 nm to 875 nm (several plots of $\ln(<P>_{\text{th}})$ versus $\ln(v)$ are shown in ). From 725 nm to 800 nm the value of $n$ appears to rise from 2.19 to 2.94 which means the absorption mechanism is changing from a two-photon absorption to a three-photon absorption. At wavelengths longer than 800 nm, the value of $n$ appears to stay around 3.0. This plateau is indicative of the bandwidth of the three-photon absorption, which is at least $\sim$100 nm. In theory, even longer wavelengths than 875 nm would result in larger values of $n$, however this could not be tested at this time due to the limited capability of the Mira.

Table 5.1. Value of $n$ at various wavelengths determined by suspended line scan fabrication.

<table>
<thead>
<tr>
<th>$\lambda$ / nm</th>
<th>$n$</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>725</td>
<td>2.19</td>
<td>0.06</td>
</tr>
<tr>
<td>750</td>
<td>2.31</td>
<td>0.06</td>
</tr>
<tr>
<td>775</td>
<td>2.50</td>
<td>0.01</td>
</tr>
<tr>
<td>800</td>
<td>2.94</td>
<td>0.09</td>
</tr>
<tr>
<td>825</td>
<td>2.94</td>
<td>0.08</td>
</tr>
<tr>
<td>850</td>
<td>3.11</td>
<td>0.06</td>
</tr>
<tr>
<td>875</td>
<td>2.91</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Figure 5.7. Plot of $\ln(<P>_{th})$ vs. $\ln(<v>)$ (original units were in mW and $\mu$m s$^{-1}$, respectively) for wavelengths 725-875 nm. Each wavelength is fitted to a line where the slope of the line, is $m = 1/n$ (indicated on each line).

5.3.4. Determination of threshold average power and $n$ using amplified pulses having $\tau = 90$ fs

Amplified femtosecond pulse lasers, which are increasingly used for DLW, can deliver pulse energies on the order of hundreds of nanojoules or higher. These energies are clearly higher than those generated by CW mode-locked lasers and can activate higher-order processes. Suspended lines were fabricated using an AFS laser to compare the order of the nonlinearity at $\lambda = 800$ nm, 1 kHz repetition rate, using pulse pitches that are similar to that reported by Seet et al. Pulse pitches 1 to 128 nm were done using scan speeds in accordance to Equation. 2.34. The data resulting from the AFS line scan experiment is shown in Figure 5.8. From the given slope
of line, the value of $n$ at the given conditions are $3.1 \pm 0.2$, which does not appear to support an impact ionization absorption mechanism (where $n = 4$).

**Figure 5.8.** Plot of line width vs. average power at difference scan speeds using the AFS source at 800 nm and a pulse duration of $\tau = 90$ fs.
Figure 5.9. Plot of ln(<P>_{th}) vs. ln(ν) from an AFS suspended line scan at 800 nm. The slope corresponds to $n = 3.1 \pm 0.2$

5.3.5. *Determination of two-photon absorption cross-section and order of non-linear absorption with Z-scan measurement*

The solvent to dissolve the PAG in for the Z-scan measurement was chosen based on several criteria. High solubility is the most important because the PAG mixture does not have high non-linear absorption strengths, thus a high concentration of the PAG mixture was needed. The solvent itself should ideally not have any linear or non-linear absorbance as well. An additional criterion was that the solvent should have a similar solvent polarity as the SU-8 matrix. Solvent polarity is general term used to describe the numerous specific (such as hydrogen bonding) and non-specific (such as dipole-dipole) interactions that occur between the solvent and
solute molecules [122]. A large change in these solvent interactions would lead to different conclusions if the molecules’ behavior being studied is sensitive to these interactions. Even absorption behavior should be no exception.

To address this possibility, UV-Vis of the solutions of the PAG mixture diluted from 50 wt-% to roughly 0.12 wt-% was done to evaluate the solvatochromic behavior of the PAG mixture. The solvent polarity of the SU-8 matrix (without PAG) was evaluated by dissolving Reichardt’s dye (Aldrich, CAS #10081-39-7) in the SU-8, spin coat processing the solution into a film, and observing the peak of the dye’s longest wavelength band by UV-Vis. Both results are shown in Figure 5.10. From the UV-Vis spectra, the longest wavelength band of the PAG mixture appears to be around 300 nm and only shifts ~10 nm when going from methanol, having the high solvent polarity, to tetrahydrofuran, having a low solvent polarity. Low polarity solvents Ether and toluene (E_T^N values of 0.117 and 0.099, respectively) did not fully dissolve the PAG mixture even at concentrations of 0.1 mM, but their observed bands were also around 300 nm amounts. The PAG mixture was virtually insoluble in hexane (E_T^N = 0.009). In Table 5.2 are listed E_T^N values of the solvents which includes the result of SU-8 matrix. The value of SU-8 shows its solvent polarity is between that of propylene carbonate and methanol. Combined with the small shift of the ~300 nm band at even larger changes of polarity, it can be qualitatively reasoned that propylene carbonate and SU-8 film will have similar interactions with the PAG mixture.
Figure 5.10. UV-Vis spectra of the PAG mixture in solvents of various polarity.

Table 5.2. $E_{T}(30)$ and $E_{T}^{N}$ values of various solvents and SU-8 matrix

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_{T}(30)$ (kJ mol$^{-1}$)</th>
<th>$E_{T}^{N}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>55.4$^{a}$</td>
<td>0.762$^{a}$</td>
</tr>
<tr>
<td>SU-8 matrix</td>
<td>49.3</td>
<td>0.57</td>
</tr>
<tr>
<td>propylene carbonate</td>
<td>46.0$^{a}$</td>
<td>0.47$^{a}$</td>
</tr>
<tr>
<td>dimethyl sulfoxide</td>
<td>45.1$^{a}$</td>
<td>0.444$^{a}$</td>
</tr>
<tr>
<td>chloroform</td>
<td>39.1$^{a}$</td>
<td>0.259$^{a}$</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>37.4$^{a}$</td>
<td>0.207$^{a}$</td>
</tr>
</tbody>
</table>

$^{a}$ Values of solvents are from Chem. Rev. 94, 2319 (1994).
In Figure 5.11 are example Z-scan traces of the PAG mixture at similar incident power but at different wavelengths. As the wavelength is increased, the overall absorbance of the sample is decreased which is correlated with a decrease in non-linear absorptivity with longer wavelength radiation. In Figure 5.12 is a plot of log($T_{min}$) versus log($<P>$) for selected wavelengths. Each of the plots correlate very well to lines with slopes at or around one, which correspond to $n = 2$. The uncertainty in $n$ based on the standard error of the fitted slope is in the range of ±0.1. In Table 5.3 is a summary of $n(\lambda)$ measured by Z-scan, where it can be concluded that the PAG mixture absorbs light via two-photon absorption at wavelengths between 500-700 nm.

![Z-Scan traces with wavelengths and incident powers indicated](image)

**Figure 5.11.** Example Z-Scans with their wavelengths and incident powers indicated. The minimum transmittance at $z = 0$ generally decreases with longer wavelengths to where it is marginally observed ($T_{min} = 0.98$) at 800 nm.
Figure 5.12. Plot of log(1 – $T_{\text{min}}$) vs. log($<P>$) (original units were in mW) for wavelengths 600-700 nm. Each wavelength is fitted to a line where the slope of the line, is $m = n - 1$ (indicated on each line)
Table 5.3. Value of $n$ at various wavelengths determined by Z-scan

<table>
<thead>
<tr>
<th>$\lambda$ / nm</th>
<th>$n$</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1.89</td>
<td>0.03</td>
</tr>
<tr>
<td>525</td>
<td>1.94</td>
<td>0.04</td>
</tr>
<tr>
<td>550</td>
<td>1.80</td>
<td>0.05</td>
</tr>
<tr>
<td>575</td>
<td>1.86</td>
<td>0.07</td>
</tr>
<tr>
<td>600</td>
<td>1.82</td>
<td>0.03</td>
</tr>
<tr>
<td>625</td>
<td>2.02</td>
<td>0.04</td>
</tr>
<tr>
<td>650</td>
<td>1.92</td>
<td>0.02</td>
</tr>
<tr>
<td>675</td>
<td>1.97</td>
<td>0.05</td>
</tr>
<tr>
<td>700</td>
<td>2.18</td>
<td>0.03</td>
</tr>
</tbody>
</table>

With 800-nm light, the absorptivity is almost negligible and a noisy Z-scan trace is observed. The power was increased to improve the signal to noise however other non-linear mechanisms became quickly apparent which ultimately did not improve the quality of the Z-scan trace. Taking the usable Z-scan traces at 800 nm a value of $n \sim 3.0 \pm 0.4$ was found. This is clearly shows hyper quadratic power dependence, but it is not of sufficient quality to obtain a 3PA cross-section or more precise value of $n$. So data suggests cubic but not definitive in and of itself. This is mainly due to a very small window in available incident power between measurable 3PA absorption and additional non-linear effects that our experimental setup could
not account for. Other wavelengths active for 3PA could not be explored due to lack of enough energy from the laser system.

5.3.6. *Theoretical multi-photon absorption calculation of PAGs*

The calculated 1PA, 2PA, and 3PA spectra of the mono- and bis-sulfonium molecules are shown in Figure 5.13. Comparing the 1PA spectra of both molecules (Figure 5.13a/a’), the 180-nm band can be assigned to the \( \pi-\pi^* \) transitions of the pendant phenyl rings, and the band is more intense for bis-sulfonium, because it has twice as many aromatics rings than the mono-sulfonium. The longest wavelength band of the bis-sulfonium at 292-nm is slightly red-shifted compared to that of the mono-sulfonium at 285 nm due the extended \( \pi \)-conjugation of the former. Comparing the 2PA spectra of both molecules (Figure 5.13b/b’), the bis-sulfonium has three bands centered on 220 nm, 250 nm, and 280 nm, while the mono-sulfonium has only two bands centered on 200 nm and 260 nm. The additional band on the bis-sulfonium can be attributed to its addtional sulfonium center that increases the overall charge-transfer character of the excitation. Comparing the 3PA spectra (Figure 5.13c/c’) of the two molecules, their bands appear roughly similar, except for the slight shoulder seen at 250 nm band for mono-sulfonium. All three 1PA, 2PA, and 3PA spectra of the bis-sulfonium have larger cross-sections relative to those of the mono-sulfonium, which is also attributed to larger charge transfer present in the bis-sulfonium.
Figure 5.13. Mono-sulfonium a) 1PA, b) 2PA and c) 3PA theoretical spectra. Bis-sulfonium a’) 1PA, b’) 2PA and c’) 3PA theoretical spectra. Stick spectra scale (center of the figure) and Lorentzian convolution scale (left and right of the figure) are shown. All spectra are plotted vs. 1PA wavelength. The units of $\sigma^{(2)}$ and $\sigma^{(3)}$ are in $10^{-50}\text{ cm}^4\text{ s photon}^{-1}\text{ molecule}^{-1}$ and $\text{cm}^6\text{ s}^2\text{ photon}^{-2}\text{ molecule}^{-1}$, respectively.
Figure 5.14 is a comparison of the calculated 1PA and 2PA spectra compared with the experimental spectra obtained from Z-scan measurements. The experimental 1PA spectra (UV-Vis), are that of the PAG mixture dissolved in propylene carbonate at 0.12 wt-%. The absorption strength measured in UV-Vis appears to agree better with the mono-sulfonium than for the bis-sulfonium, which suggests that there is a greater content of the mono-sulfonium in the PAG mixture. The 2PA spectra also appear to agree well with that of the mono-sulfonium, with a single band appearing at ~300 nm, and a second that only begins to appear around 250 nm. The slight shoulder observed at ~315 nm can originate from contributions of the bis-sulfonium. It should be noted that there is a noticeable difference in amplitude and wavelength between the calculated and experimental spectra. The difference in amplitude between the theoretical and experimental spectra could be attributed to exciton coupling [123]. There is also a disagreement in the wavelengths which is very likely due to not including solvent effects in the calculation. Although few conclusions can be given through direct comparison of amplitudes and wavelengths, the general shape of the bands can still be compared. The theoretical spectra in Figure 5.14 were shifted in amplitude (by a factor of ~15) and wavelength (by +30 nm) which was useful in comparing the relative changes in absorption strength versus wavelength.
Figure 5.14. Calculated 1- and 2PA spectra of the mono- and bis-PAGs compared to the experimental 1PA spectrum (measured by UV/Visible spectrophotometry) and 2PA spectra (measured by Z-scan) for the PAG mixture. The theoretical spectra were obtained by convoluting the calculated transition probabilities with a Lorentzian line-broadening function having a FWHM of 0.8 eV and 0.2 eV for the 1PA and 2PA transitions, respectively. The 1PA and 2PA spectra were shifted by +10 nm and +30 nm, respectively, [124] to aid in the comparison of the general trend with that of the experimental data. The units of $\sigma^{(2)}$ are in $10^{-50}$ cm$^4$ s photon$^{-1}$ molecule$^{-1}$. 
A weighted 2PA spectrum was calculated using a PAG composition of 83% mono-sulfonium and 17% bis-sulfonium, shown in Figure 5.15. The PAG composition was determined from elemental analysis (Section 2.3.4). The result of the analysis is listed in Table 5.4, which show that the PAG mixture is mostly composed mono-sulfonium. The main two bands, observed at approximately 240 nm and 280 nm, are originated by the major contribution from transitions 26-36 and 5-7 in the mono-sulfonium, and a minor contribution from transitions 59 and 7 in the bis-sulfonium. The shoulder observed at 315 nm is mostly from the strong contributions of transitions 4 and 5 in the bis-sulfonium, and the minor contributions of transitions 2 and 3 in the mono-sulfonium. Regardless, the shape of the weighted spectra is very similar to that of the experimental spectra.

**Table 5.4.** Results of fluorine and sulfur mass analysis of the PAG mixture (Aldrich) and SU-8 2075 (MicroChem).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( w_F ) (wt-%)</th>
<th>( w_S ) (wt-%)</th>
<th>( x_{\text{bis}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAG mixture</td>
<td>9.11 ± 0.11</td>
<td>4.76 ± 0.12</td>
<td>0.17 ± 0.10</td>
</tr>
<tr>
<td>SU-8 2075</td>
<td>0.6699 ± 0.0082</td>
<td>0.3588 ± 0.0093</td>
<td>0.11 ± 0.10</td>
</tr>
</tbody>
</table>

Elemental analysis was also performed on SU-8 2075, which was also found to be mostly composed mono-sulfonium. Within error, the PAG ratios of both samples being studied are similar, which is an important consideration because data from both Z-scan (on the PAG mixture) and suspended line scan (on the photoresist) are analyzed together in Section 5.3.7.
Figure 5.15. Calculated 2PA spectra of the PAG mixture compared to experimental 2PA spectra (measured by Z-scan). The theoretical spectra were obtained by convoluting the calculated transition probabilities (scaled by a 0.83 and 0.17 factor for mono- and bis-sulfonium, respectively) with a Lorentzian line-broadening function having a FWHM of 0.2 eV. The spectra were shifted by +30 nm [124] to aid in the comparison of the general trend with that of the experimental data. The units of $\sigma^{(2)}$ is $10^{-50}$ cm$^4$ s photon$^{-1}$ molecule$^{-1}$.

5.3.7. Comparative analysis of spectroscopic and line-scan data

Figure 5.16 is a plot of $n$ for 725-875 nm using suspended line scan, and 500-700 nm using Z-scan. The plot shows the value of $n$ is initially 1.9 at 725 nm, begins to increase around 700 nm, and plateaus around 3.0 at 800 nm. The PAG mixture in SU-8 is activated primarily by 2PA from 600 nm - 700 nm and 3PA from 800 nm - 875 nm. The apparent non-integer value between the 700 nm - 800 nm implies that over this range of wavelengths the material is being
excited by both 2- and 3PA processes. However, because 2PA and 3PA have different dependence on flux, the specific value of $n$ should not be used to infer a relative contribution of the two processes at a given wavelength. In principal, the rate of 3PA could be increased, and thus the measured value of $n$ could be increased, by performing the experiment using higher incident laser power. In practice, the range of laser powers that can be used is limited on the low end by the ability to detect signal over background, and on the high end by damage to the sample. The result then is that $n$ appears to change monotonically from two to three across a spectral region where both excitation mechanisms are active. Mixed 2PA and 3PA has observed in bulk rutile [125].

![Figure 5.16](image)

**Figure 5.16.** Plot of $n$ as a function of laser wavelength from Z-scan (black squares) and suspended line scan (red circles) the error bars represent the standard error of the line fits.
5.3.8. Determination of threshold average power and order of the nonlinear absorption using amplified pulses having elongated pulses of $\tau = 180$ fs

One noted difference with our experiment is that the pulse duration used in this experiment is 90 fs, as opposed to 180 fs. Laser ablation of glass and silicon substrates with pulsed lasers show that pulse duration can affect the competing the absorption mechanisms, impact ionization and multi-photon ionization [92, 126, 127]. Assuming that both mechanisms have a different value of $n$ this would mean that $n$ can change with pulse duration, even in the mpDLW of polymeric resists. This was tested by repeating the line scan experiment at the same conditions except the pulse duration being extended to $\tau = 180$ fs. The resulting measured line widths are shown in Figure 5.17, which are also fitted to a Gaussian focus. The $\ln(<P>_m)$ vs. $\ln(\nu)$ plot in Figure 5.18 reveals that the value of $n$ is $3.8 \pm 0.2$, which are significantly greater than 3.1. This confirms that long pulse duration can affect the value of $n$, which corresponds to a previously minor absorption processing becoming dominant. Z-scan measurements of $n$ for the PAG mixture

Although the measurements discussed above are internally consistent, they do differ from the value of $n = 4$ reported by Seet et al. [59]. One notable difference between the experiments discussed here and those reported by Seet et al. is that they used AFS laser pulses that were 180 fs, which is twice as long as those used for the work discussed here. Studies of laser ablation in glass and silicon show that pulse duration plays an important role in determining which mechanisms dominate the light-matter interaction, including impact ionization and multi-photon ionization [92, 126, 127]. Assuming that both mechanisms have a different value of $n$ this would mean that $n$ can change with pulse duration, even in the mpDLW of polymeric resists. The
effect of pulse duration was examined on $n$ was tested by repeating the line-scan experiments under the same conditions except that the pulse duration was extended to $\tau = 180$ fs. The resulting measured line widths are shown in Figure 5.17. The $\ln(<P>_{th})$ versus $\ln(v)$ plot in Figure 5.18 reveals that the value of $n$ is $3.8 \pm 0.2$, and is significantly greater than 3.1. This confirms that long pulse duration can affect the value of $n$, which corresponds to a previously minor absorption processing becoming dominant. Seet et al. argue that the value of $n = 4$ results from an avalanche ionization mechanism in which a critical density of electrons are ionized from the electric field and form a plasma [128]. The plasma heats a localized volume of the SU-8 above the thermal stability of the PAGs (releasing acid) [129]. Seet et al. reported that in certain conditions, the laser annealing can provide enough heating to polymerize the exposed SU-8 without the required post-exposure bake step. The mechanism of the plasma heating is not exactly known; however Seet et al. argue that the heating occurs via the spectrally broad blackbody-type emission in the IR generated by the plasma. The emission is then directly absorbed by the SU-8 matrix in the 2-3 $\mu$m wavelength range. The Stephen-Boltzmann law that relates the rate of emitted energy and temperature gives the thermal dependence as fourth order, which is functionally similar to the fourth order power dependence observed in experiments.
Figure 5.17. Plot of line widths as a function of average power at various scan speeds, using the AFS source and pulse duration of 180 fs.

Figure 5.18. Plot of $\ln(<P>_t)$ vs. $\ln(v)$ using the AFS source at 800 nm and pulse duration 180 fs. The fitted slope corresponds to $n = 3.8 \pm 0.2$. 
5.4. Conclusion

The order of absorption process as a function of wavelength was determined by fabricating suspended line features in SU-8. The increase of $n$ from 2.2 to 3.2 between wavelengths 725-875 nm can be argued as a mixture of two- and three- photon absorption processes that dominate at either end of the spectrum. This alternation of $n$ is corroborated with theoretical multi-photon spectrum calculation and supplemental Z-scan measurements which imply that there can be overlap between the 2PA (toward longer wavelengths) and 3PA (toward shorter wavelengths) spectra. Equations show that the value of $n$ can be determined by observing how the threshold average power of line features can vary as a function of scan speed. Fabricating features in the same manner with an amplified femtosecond system at 800 nm has yielded a similar result, although observing higher order absorption processes such as avalanche absorption may require higher irradiances or longer pulse durations.
6.1. Introduction

The continuing transition from electronic to photonic telecommunications, information processing, and sensing has been enabled in large part by the inherent advantages of optical waveguiding by optical fibers. Further advances are expected to make increasing use of truly integrated photonic devices that do not require opto-electro-optical interconversion or bulky interconnects. To facilitate such advances, new approaches and material systems are needed for creating two- and three-dimensional integrated photonic devices, particularly those that can leverage existing technologies in fiber optic and electro-optic device fabrication. Numerous approaches have been reported for integrating refractive and diffractive optical devices with optical fibers. Few, however, are suitable for fabrication of arbitrary three-dimensional optical elements directly onto optical fibers [130, 131]. Multi-photon direct laser writing (DLW) has been used to fabricate functional optical elements on side-polished optical fibers [132] and cleaved end faces [133] using liquid photopolymer resins.
SU-8 is commonly spin coated on substrate and bake to remove solvent. This particular step of casting SU-8 is not practical or even feasible on optic fibers. Therefore the typical processing steps of casting, exposing, and developing must be modified in the case of fabricating structures on single optic fibers. In the modified approach, solvent is removed from a bulk amount of SU-8 resin (~10 mL) by heating in vacuo. The resulting solid material is then melt-reflowed around the optical fiber in a mould and allowed to cool. Upon cooling, the solidified resin immobilizes the optical fiber, so the entire sample can be affixed to a fabrication system and patterned. A wide array of structures can be fabricated on a fiber tip as shown in Figure 6.1. Optical fibers bearing conventional refractive elements can be readily prepared, including radially symmetric convex and concave lenses (Figs. 1A – 1C) and cylindrical lenses (Figs. 1D – 1E). Truly three-dimensional structures with complex topology and undercut can also be fabricated, such as multi-lens systems (Figs. 1F – 1H) and "woodpile" photonic crystals (Figs. 1I – 1K), that would be impossible to create by other existing methods.
Figure 6.1. False-color SEM images of micro-structures created on the end of an optical fiber by DLW in SU-8 resin. (A - C) Plano-convex lens having radius of curvature $R = +18.3 \, \mu m$ viewed (A) down the fiber axis and (B, C) from the side. (D, E) Cylindrical lens having $R = +15.7 \, \mu m$. (F - H) Compound micro-optic system consisting of a suspended plano-convex lens having $R = +29.5 \, \mu m$ and a smaller plano-concave lens in contact with the fiber end-face having $R = -23.1 \, \mu m$. For the structure shown in (G) and (H), only the first and third quadrants of the negative lens were fabricated so the internal curvature could be seen clearly. (I - K) A woodpile face-centered tetragonal photonic crystal.
6.2. Discussion

6.2.1. Processing and microstructure fabrication

The structures prepared include simple plano-convex lenses, a cylindrical lens, a compound lens system, and a woodpile photonic crystal structure. Plano-convex lenses were prepared with a targeted radial curvature of $R = +20 \mu\text{m}$ (Figure 6.1A) and $R = +40 \mu\text{m}$ (not shown). The actual structures were found to have lens curvatures of $R = +18.3 \mu\text{m}$ and $R = +34.7 \mu\text{m}$, respectively. The compound lens system was fabricated with targeted positive- and negative-lens curvatures of $R = +34 \mu\text{m}$ and $R = -20 \mu\text{m}$. The actual curvatures were found to be $R = +29.5 \mu\text{m}$ and -23.1 \mu{m}. Differences in curvature between the targeted and actual structures are thought to result primarily from resin re-flow occurring during the post-exposure bake, which could be reduced by optimizing the post-exposure process. Although the fidelity of the fabrication was not optimized, we found that the optical performance was reproducible when a given structure was fabricated multiple times.

Viewing down onto the end face of the optical fiber (Figure 6.1A) confirms that the micro-optics can be fabricated well centered with respect to the fiber, and thus well overlapped with the core. Side views of the cylindrical lens (Figure 6.1D and E) show that the serial patterning process enables the radius of curvature along the fast and slow (non-focusing) axes to be defined independently. Additionally, by simply rotating the coordinates of the structure file, the orientation of these axes could be set with respect to those of a radially anisotropic surface, such as a polarization-preserving fiber.

The compound-lens structure was created in a single serial exposure by patterning the smaller plano-concave optic in contact with the fiber end-face and the plano-convex optic
suspended by four supports, so the two lenses are separated by an air-gap. A variant of this device was created with quadrants one and three of the negative lens purposefully omitted so its concavity would be clearly visible (Figure 6.1F-H). The length of the supports could be altered to vary the separation between the micro-optics and thereby vary their collective focusing properties. The woodpile structure (Figure 6.1I-K) provides an extreme example of how the method can be used to create new integrated photonic devices consisting of micro-optical structures with a high degree of undercut and topological complexity. Collectively, these examples illustrate the power of this method for creating truly 3D structures in SU-8 directly on the end-face of an optical fiber.

6.2.2. Processing and micro-structure fabrication

During the melt-reflow process itself, the optical fiber can laterally shift as the molten resin flows around the fiber, however this shift is small provided the fiber is not physically disturbed during the casting step. Air bubbles can also form within the resin as it fuses and traps air (Figure 2.5C). Bubbles can be minimized by using large pieces for the melt-reflow. Ten minutes of melt-reflow proved sufficient for bubbles to migrate to the surface and burst, for the resin meniscus to settle to its final shape, and for the fiber to relax back its aligned position within the SU-8 well. Overall, this casting process is typically no longer than 30 minutes. Because the resin solidifies around the optical fiber, it cannot move during photo-patterning, as is the case for liquid-resin approaches [132, 133]. This provides an inherent advantage for precision micro-fabrication onto optical fibers.
6.2.3. **Characterization and performance of vacuum-baked-resin**

\textsuperscript{1}H-NMR analysis showed that the solvent content of SU-8 2075 resin as supplied was 19 mass-percent. The solvent content dropped rapidly with heating \textit{in vacuo} and could be reduced to nearly one mass-percent in as little as one hour. Significantly longer heating was needed to reduce the solvent content further, as the molten, low-solvent resin is highly viscous. A solvent content of 0.68 mass-percent was achieved with overnight heating (14 hours).

The woodpile structure proved useful for evaluating the fabrication process and how solvent content and other parameters affect structure fidelity. This particular structure is intricate, having features with sizes on the order of a micron, so it will not be self-supporting if the degree of cross-linking, and consequently the mechanical robustness, are poor. Figure 6.2 shows SEM images of woodpile structures prepared by DLW using vacuum-baked resin heated for one, three, and fourteen hours, and viewed normal to the supporting substrate. The highest quality structure is obtained when prepared using resin-solids heated for 14 hours. In that case, the feature-edge contrast is high, the features are least rounded, the interior of the structure is least filled in, and the crossing points of overlapping "logs" are most sharply defined. This suggests that low solvent content helps confine the polymerization reaction and thus improves the patterned structure integrity, possibly by limiting acid diffusion or resin reflow that can occur during the post-exposure bake. These observations are consistent with earlier reports of how solvent content affects performance of liquid SU-8 resin that is spin coated and soft-baked in the customary way for DLW, conventional photo-lithography, X-ray, or e-beam patterning of micro- and nano-scale devices [24, 53, 134-137].
Figure 6.2. Effect of residual solvent on the fidelity of woodpile structures created by DLW in SU-8 on the end-face of an optical fiber. (Left) Graph of solvent mass-percent versus time for which the resin was heated in vacuo. (Right) Top-view SEM images of woodpile structures prepared by DLW using resin solids heated in vacuo for the specified time. All scale bars correspond to 5 \( \mu \)m.

We examined the possibility of dispensing SU-8 2075 as a liquid directly into the sample mould and around the pre-hung fiber and then baking the sample mount to drive off solvent. This did yield a solid resin plug with good optical quality. But mpDLW experiments produced poorly defined structures with low structural integrity that did not survive the developing step. \(^1\)H-NMR analysis showed that the solvent content of the resin plug produced in this way remained high, generally above five mass-percent, even with protracted periods of baking, up to
24 hours at 110 °C. We reason that solvent evaporation is hindered by the restricted volume, low exposed surface area, and comparatively large thickness of the resin droplet, leaving the melt-reflow process as the preferred approach. Other investigators have encountered similar difficulty when attempting to fabricate in ultra-thick (~1 mm) slabs of SU-8 cast from the liquid resin [135] [120] [97]. Becnel and co-workers conclude that a low-solvent skin forms at the resin-air interface during the pre-exposure bake that hinders solvent release from the underlying bulk. Various approaches have been proposed for surmounting this problem, including a multi-layer casting and "dry chip casting" [120]. Denning and co-workers used a "hot-casting" approach to study shrinkage of specially formulated SU-8 from which low-molecular-weight fractions of the epoxide oligomer had been removed [53]. These casting methods are similar to the melt-reflow approach used here.

Another consequence of processing in very thick films is that there is significant temperature gradient from the hotplate to the surface of the film. As such, temperatures that are measured from the hotplate sensor did not correspond to the temperature of the SU-8 film, resulting in suboptimal baking temperatures and undercross-linked features. A small thermistor bead was immersed in the SU-8 well and confirmed that the temperature was 20 °C lower than the recommended bake temperature of 95 °C. This discrepancy was easily corrected by increasing the hotplate temperature to 115 °C which was confirmed to give the targeted bake temperature in the SU-8 well.
6.2.4. Optical characterization and performance of microlenses

A summary of the theoretical and experimentally measured parameters of the lenses and output beam is shown in Table 6.1. A plot of FWHM (\(\sim 1.18w(z)\)) for several of the micro-optic tipped fibers is shown in Figure 6.3. From the figure, it can be seen that the microlenses cause the beam to have a higher divergence angle compared to that of the bare fiber. In Table 6.1 it can be seen that the divergence angle is increased with a lower radius of curvature. This is also observed in the x-axis of the planoconvex lens having the lowest radius of curvature. The beam radius on the y-axis of the planoconvex lens is similar to that of the bare fiber as expected. This means that the microlenses brings the fiber output into a focus near the end-face, and proceeds to diverge at a greater angle than that of the bare fiber. This observed behavior agrees with that of the simulated beam width as a function of distance from the end face.
Table 6.1. Calculated and observed characteristics of microlenses fabricated on the end face of a single-mode fiber by DLW in SU-8. Lens performance was measured using 633 nm light as input source. PC = Plano-convex lens, CYL = cylindrical lens, $R$ = Radius of curvature. Observed performance from a bare fiber are included for comparison. Values of beam width from a PC are shown as an average of the x- and y-axes. Beam ellipticity is expressed as a ratio of $w(z)$ measured along the orthogonal axes.

<table>
<thead>
<tr>
<th>Microlens parameters</th>
<th>Bare Fiber</th>
<th>PC Lens #1</th>
<th>PC Lens #2</th>
<th>CYL Lens</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$, observed</td>
<td>--</td>
<td>34.1 μm</td>
<td>18.3 μm</td>
<td>15.7 μm</td>
</tr>
<tr>
<td>$R$, targeted</td>
<td>--</td>
<td>40.0 μm</td>
<td>20.0 μm</td>
<td>10.8 μm</td>
</tr>
<tr>
<td>Peak-height of lens</td>
<td>--</td>
<td>4.3 μm</td>
<td>9.4 μm</td>
<td>3.8 μm</td>
</tr>
<tr>
<td>$w(z = 15 \text{ mm})$</td>
<td>x-axis</td>
<td>y-axis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observed (FWHM)</td>
<td>1.44 mm</td>
<td>1.76 mm</td>
<td>2.07 mm</td>
<td>2.30 mm</td>
</tr>
<tr>
<td>Calculated (FWHM)</td>
<td>--</td>
<td>1.57 mm</td>
<td>1.82 mm</td>
<td>2.10 mm</td>
</tr>
<tr>
<td>Observed ($e^{-2}$)</td>
<td>1.23 mm</td>
<td>1.49 mm</td>
<td>1.76 mm</td>
<td>1.95 mm</td>
</tr>
<tr>
<td>Calculated ($e^{-2}$)</td>
<td>--</td>
<td>1.33 mm</td>
<td>1.55 mm</td>
<td>1.79 mm</td>
</tr>
<tr>
<td>Divergence angle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observed</td>
<td>0.082 rad</td>
<td>0.099 rad</td>
<td>0.12 rad</td>
<td>0.13 rad</td>
</tr>
<tr>
<td>Calculated</td>
<td>--</td>
<td>0.088 rad</td>
<td>0.10 rad</td>
<td>0.12 rad</td>
</tr>
<tr>
<td>Beam ellipticity</td>
<td>1.03</td>
<td>1.02</td>
<td>1.02</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Lee and Barnes used conventional lithography to create hemispherical microlenses on the end of single-mode fibers and experimentally characterized their focusing [138]. Lee modeled the focusing using the paraxial Gaussian beam approximation (also applied here), and compared the results to those obtained using Fresnel diffraction theory [139]. The position of the maximum intensity and minimum beam size differ by less than 10% when the ratio of the lens radius to beam size at the fiber end-face, $r_0/\omega_0$, is 1.65 and 1.8, respectively. Values calculated with both levels of theory for a given focusing parameter converge for $r_0/\omega_0 > 3$. For the
structures fabricated here, \( r_0/\alpha_0 > 5 \), so the use of the paraxial theory is satisfactory, and it cannot be the source of difference observed between calculated and experimental beam parameters. Lee also showed that lens aberration impacts the focusing parameters significantly more than the level of theory used to describe them. The differences observed between theory and experiment are most likely due to imperfections in the microlens shape.

**Figure 6.3.** Beam width versus distance, \( z \), from the end face of optical fibers bearing refractive lenses created by multi-photon direct laser writing in SU-8. The label "CYL" indicates a cylindrical lens, whereas "PC" indicates a plano-convex lens. Values preceding these labels specify the lens radius of curvature in microns. Beam width measurements for a bare fiber are included for comparison. Measurements made parallel to the \( x \)- and \( y \)-axes are represented by filled and hollow symbols, respectively.
Given that the internal volume and surface of the micro-optics are defined by photo-exposure along an array of lines, one might expect they would be partially diffractive or highly scattering. Close inspection of the microstructures shown in Figure 6.1 show that their surfaces are actually smooth in the micron length scale. Additionally, their imaged beam profiles do not show significant scatter. Surface smoothness of the lenses was achieved by patterning the lenses with vertically aligned scan lines. The end of each scanned line can be pinpointed to within 5 nm. In combination with the line pitch of 5 μm, the optical surface of the lens can be defined smoothly. Further smoothing of the lens surface is expected from the overlap of the line size and diffusion of the photoacid [120]. This effectively homogenizes the volume of the lenses and far field diffraction or scatter is not observed. Despite efforts to limit diffusion, some degree of it is actually desirable as it appears to contribute to the process and improve the performance of the device. Ultimately, it would be desirable to in mpDLW to controllably exploit the effects of diffusion to benefit the design of any micro device.

Figure 6.3 shows that beam widths along the x- and y-axes are similar at a given distance for either bare fiber or one containing a plano-convex lens, thus they have nearly unity ellipticity values (Table 6.1). This result is expected for a linearly polarized light focused by a radially symmetric lens of with a low NA [11]. The fiber containing the cylindrical lens has much different beam profiles. The beam width associated with the y-axis (the slow/non-focusing axis) is very close to that obtained with the bare fiber, whereas the x-axis beam is 40% larger, and the ellipticity is much greater than unity. This is expected from a cylindrical lens and illustrates that a functional SU-8 micro-optic can fabricated on a fiber optic end-face to alter its beam output.
The reproducibility of the fabrication process was explored by producing three plano-convex lenses \((R = +20 \, \mu m)\) under identical conditions and comparing their characterized beam output. Figure 6.4 shows that beam widths of all three lenses nearly overlap all the way to \(z = 15\) mm. The maximum variation observed at \(z = 15\) mm is roughly 5\% (seen in the y-axis). This implies that there is good reproducibility in the lens fabrication.

![Graph showing beam width measurement](image)

**Figure 6.4.** Reproducibility in optical performance observed for three separate fabrications of a plano-convex lens (targeted curvature \(R = +20\) \(\mu m\)) onto the end face of an optical fiber by multi-photon direct laser writing in SU-8. Beam width measured parallel to the \(x\)-axis is plotted versus distance \(z\) from the end face of the fiber. Measurements obtained for a bare fiber are included for comparison.
6.3. Conclusion

An approach has been developed for fabricating micro-structures on the end-face of optic fibers. A compound lens and photonic crystal were prepared to demonstrate that 3D structure of high complexity can be fabricated with this method, which are otherwise difficult or impossible to make with other approaches. Characterization of the simple lens devices show that low scatter and high reproducibility can be attained. More development on this approach will center on improving fidelity, tolerance, functional complexity, and performance. Some near term routes can be on exploring the post-exposure process and/or improving the sample holder.

The simple lens structure fabricated here can be manufactured in bulk. The lens structure itself takes four minutes to pattern. Preparing the sample and baking takes considerably longer, but they can be parallelized or the lenses can be processed in batches. Even the patterning can be processed in parallel, however consider this to be the only limiting factor, 10,000 microlenses can be fabricated in approximately 30 days.

Because any complex device can be potentially fabricated, this can further expand the technology of fiber optics. High efficiency optical fiber couplers, low insertion-loss micro-laser couplers, fiber output beam shapers, and a new class of optical sensors could be realized. Fabrication of novel beam coupling devices could be a particularly fruitful application. The method could be used to create aspherics, radially asymmetric lenses, or multi-lens elements that enable more efficient fiber-coupling from sources that generate irregular beams, like laser diodes or vertical-cavity surface emitting lasers. A new class of integrated photonic devices, particularly sensors, could be realized with collective performance that was previously unachievable, including high immunity from electromagnetic interference, chemically inertness,
and the potential to operate in extreme environments interfaced electro-optically to remote driving electronics.
CHAPTER 7: SUMMARY AND OUTLOOK

This dissertation explores how processing conditions affect the size of features created in SU-8 by mpDLW. Parameters explored include pre-exposure bake duration, writing depth, and excitation wavelength. Longer pre-exposure bake-time reduces solvent content in the resin, which reduces acid diffusion during the post-exposure bake and enables fabrication of smaller features. Increased writing depth distorts the focus when there is a mismatch in refractive index between the material and the adjoining interface (air or objective oil). This effect causes the written feature-size to change with focal depth. This effect can be partly compensated by appropriate control of the laser power. By varying the scan speed and power, the order of the nonlinearity of the SU-8 resin was determined to be three at 800 nm, indicating that 3PA is the dominant excitation process at this wavelength. 2PA dominates at shorter wavelengths. These changes in the order of the excitation process are consistent with Z-scan measurements that measure the nonlinear absorption of the PAGs and calculations of the 2PA and 3PA transition probabilities.

These findings reported here can be leveraged to extend studies of SU-8 and further improve its use for high-resolution mpDLW. First, it is assumed that there is no acid diffusion that occurs during the exposure and post-exposure bake steps. To date, the effect of acid diffusion on mpDLW has not been modeled, so it remains unknown what mpDLW conditions could be used to mitigate or control its effects. If the order of the absorption, cross-section of the PAG mixture, and photoacid quantum yield were known, then the acid-concentration profile and diffusion kinetics could be accurately modeled and used to further improve mpDLW with this material system.
Second, it is not known how wavelength and its associated order of absorption affect the minimum feature size that can survive developing. Both wavelength and absorption create competing effects on the possible resolution of the feature size. Decreasing the wavelength would decrease the spot size of the beam (due to diffraction-limited focusing) but the order of the excitation would necessarily decrease from three to two, which is desirable from the standpoint of achieving high-resolution focusing and fabricating small features. On the other hand, increasing the wavelength would increase the spot size of the beam, but would increase the order of excitation as lower energy photons are absorbed. At first, this appears to be disadvantageous, but using a higher-order excitation process should result in a steeper acid-concentration gradient across the exposure volume. This may lead to increased diffusion, but it could be advantageous in terms of creating higher cross-link density within the exposed region and thus more mechanically robust features. These competing effects and how to control them could be addressed by applying the knowledge gained in this work to a coupled exposure/acid-diffusion model that uses known absorption order, cross-section, and photo-acid quantum yield. Such a study could then be used to determine the optimal processing parameters needed for creating the smallest and most robust SU-8 features by mpDLW for a given application.
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