Optimization of Direct-Write 3D Two Photon Photolithography in Poly (methyl methacrylate)

Undergraduate Research Thesis

Presented in Partial Fulfillment of the Requirements for graduation "with Honors Research Distinction in Physics" in the undergraduate colleges of The Ohio State University

by
Robert Patton

The Ohio State University
April 2015

Project Advisor: Professor Gregory Lafyatis, Department of Physics

Abstract

Direct-write multiphoton photolithography (DWMP) is a technique which exploits the localization of multi-photon processes which occur at a tightly focused femtosecond laser to write 3D patterns in a photosensitive polymer. In conventional photolithography devices are fabricated by using masks to tailor light exposure onto photo sensitive material, developing the photoresist, and this process is driven by a single photon. DWMP differs in that the energy of at least two photons is required to reach criticality for exposure chemistry. This means that whereas traditional photolithography will polymerize a material throughout the volume of the beam, DWMP will only polymerize a material where the probability of two or more photons interacting with a molecule simultaneously is incredibly high, i.e. at the focus. This is the essential idea behind DWMP which allows arbitrary 3D shapes to be created, in contrast to traditional photolithography where devices are produced in layers with strict limitations on complexity.

DWMP also allows for the creation of very small, high resolution shapes. This is possible because of the tight laser focus which produces "voxels" (volume-pixels) of polymerized material. To zeroth order the dimensions of a voxel can be estimated by a Gaussian laser's diffraction limit. However in the DWMP case, because two or more photons must interact at the beam waist to induce polymerization the effective volume is reduced in proportion to the number of photons required for the interaction. This reduces the effective volume further as a function of the cross-sectional intensity, allowing for voxels smaller than the diffraction limit.

The majority of DWMP work to date has used negative photoresists, in which exposed material is made less soluble. This results in solidified material where the focus was scanned and is useful for creating high resolution freeform structures. Here we explore and attempt to optimize DWMP with regards to the positive resist Poly (methyl methacrylate) (PMMA) using short

wavelength (~387 nm) light. Not only is PMMA a widely used and durable material in the biological community, but because it is a positive resist it is the exposed rather than unexposed material which is removed upon development. This property combined with the complexity allowed by DWMP should make it possible to make wells and intricate channels imbedded on all sides within a block of PMMA. Such a technique would prove useful in the creation of arbitrary microfluidic devices, as are often needed for biological research. We find that the technique is indeed viable while outlining a general method and defining future work to optimize the resolution of the process.

Acknowledgments

First and foremost I would like to thank Dr. Gregory Lafyatis, my research advisor, for all of his guidance and support. Dr. Lafyatis has not only been fundamental in the design and completion of this project but has also served as an invaluable mentor on matters of research and academia throughout my undergraduate career.

Special thanks are due to Dr. Enam Chowdhury who provided the space and tools with which this project was conducted as well as assistance and instruction throughout the process. I would also like to thank the graduate students Drake Austin and Kyle Kafka who assisted in the creation and operation of the multiphoton setup.

Introduction

Fabrication at the micro scale using femtosecond lasers was first popularized as an ablative process (removal by vaporization) in the mid-90s [1]. Since then the push for increasingly small and complex microstructures has led to the development of several new techniques, of which optical breakdown and nonlinear process are especially noteworthy. Because these processes take place only at the focus of the beam arbitrary 3D patterns, including ones with interlocking pieces, can be created easily without the use of masks or multi-beam interference. Optical breakdown is useful in photonics applications, where changes in the index produced by femtosecond laser fabrication are often used to create waveguides [2]. Similar techniques can be used to create filters, resonators, photonics crystals, and gratings [3, 4]. Nonlinear (multi-photon) processes excel when high resolution and arbitrary structure design are required. The use of nonlinear polymerization allows traditional resolution limitations based on the diffraction limit to be overcome. This kind of fabrication technique is highly desirable when creating microelectromechanical systems (MEMS) [5]. In addition to the variety of uses already being explored there are many fields which could potentially benefit from these techniques: nano surgery, material processing, and rapid prototyping to name a few.

Multiphoton lithography is a highly adaptable technique which can pattern organic and inorganic polymers, plastics, and even metals [6]. The mechanism by which this is accomplished generally falls into one of four categories; photoinitiated polymerization, photocleavage, photoreduction (in metals), and photochromic reactions. The two mechanisms most relevant to micro scale fabrication are photoinitiated polymerization, in which the photon energy causes two or more monomers to polymerize into a new molecule, and photocleavage, in which the photon energy breaks a molecular bond producing two or more smaller molecules. A substrate which

undergoes photocleavage in the presence of a certain radiation will tend to become more soluble. In this case the exposed region will be removed during the development process, and the substrate is referred to as a positive resist. On the other hand if the exposed region is subject to photoinitiated polymerization it will tend to solidify and remain after development, in which case it is a negative resist.

To date a large portion of the work done specifically with 3D structuring has been accomplished using negative resists, especially SU-8 [7]. Direct-write multiphoton lithography (DWMP) when used in conjunction with a negative resist is essentially an additive process, where the structure is built up using the laser focus. A major benefit of using this type of resist is that structures can be made extremely quickly, especially relative to positive resists. In positive resists such as poly (methyl methacrylate) (PMMA) the focus denatures the material in a reductive manner, similar to carving. Because of its lack of applicability to freestanding 3D microstructures PMMA represents a largely unexplored target for DWMP.

An example of typical optical work with PMMA would be micro patterning with picosecond and femtosecond lasers [8]. In this instance PMMA was shown to be a viable material for 3D optical recording. Of key interest is that femtosecond pulses of 400 nm light were used to modify the index of already cured PMMA (by creating defects) in a regular fashion. This study also examined picosecond laser processes at 532 nm and found an associated damage threshold of ~4 MW/cm^2. This study used a setup with a high NA and light of similar wavelength to ours, but primarily focused on the damage threshold since already cured PMMA was being used with no development process

Another study of note looked specifically at DWMP in PMMA [9]. This study was aimed at the creation of microelectronic devices and examined the power dependence of feature size in

several different weights of PMMA. The study met with success and created surface features with a minimum size of ~250 nm. The optical system for the experiment was similar to ours with two primary differences: infrared (870 nm) light was used and samples were not chemically developed. Using light which is already in the blue region of the spectrum before focusing on the sample allows our system a smaller initial spot size which when properly optimized should produce features smaller than those possible using infrared light. The lack of any kind of development step is attributed to the vaporization of the photocleaved PMMA during exposure. In our work chemical development is necessary to bring out finer features, which may be due to the differences in the type of PMMA solution used.

PMMA is a visibly translucent thermoplastic which was first marketed commercially under the trademark *Plexiglas*. Because PMMA is durable, transparent, and easy to spin coat and pattern with electron beam lithography it has become a common material in the creation of devices for biological research. DWMP combined with PMMA offers a unique opportunity to make more complex devices for use in such research. PMMA has almost zero transmission in the UV spectrum so without the use of two or more photons it would be impossible to use light to depolymerize the substrate any deeper than at the surface, even when using an objective based system. However a tightly focusing femtosecond laser capable of producing two photon absorption should be able to make hollow tubes and wells inside of a PMMA block. This technique creates larger feature sizes than are possible with electron beam lithography, but is capable of patterning without altering the surface or intervening material. The creation of microfluidic devices in this manner is the primary reason for this line of inquiry.

The initial motivation for this project was the creation of nano electroporation (NEP) devices, a type of microfluidic device used to inject drugs into individual cells. Each device

consists of two rows of microscopic wells connected by thin (~100 nm) tubes. By application of a small voltage across the device drugs on one side can be pushed through the tubes into cells on the other in a controlled manner. NEP devices offer a significantly improved mortality rate and are more consistent than alternative methods. Our group has been working to develop a more reliable method for creating these nano scale structures. Currently the most reliable technique, called DNA combing, involves making the tubes by dipping prefabricated devices into a solution of DNA and chitosan. The devices are dried and used as negative molds with the hope that strands of hardened DNA will form the tubes. This method is labor intensive, time consuming, and has met with limited success. By making their production faster, reliable, and customizable these devices will become useful to a much larger audience. Through DWMP we hope to make microfluidic devices such as NEP viable resources for other groups conducting biological research.

Background

Of key importance when attempting lithography at the micro scale is the diffraction limit of light. In standard masked lithography the resolvable feature size is limited to $\lambda/2$ because of the Rayleigh diffraction limit. In a focused laser situation this can be modified by using a high numerical aperture (NA) objective lens. In this case the area of exposed material depends on the laser waist (minimum radius of the beam at the focus). For a standard Gaussian beam the waist is defined by:

$$\omega_0 = \frac{\lambda}{\pi \cdot NA} \quad (1)$$

To first order the minimum exposed area will then be $\pi\omega_0^2$, with a diameter of $2\omega_0$. This method can therefore produce features smaller than the Rayleigh diffraction limit when a NA greater than $\pi/4$ (~0.8) is used.

This kind of single photon method boasts fair resolution and is the most commonly used technique in lithography today. However it features two important drawbacks. The first is that the minimum feature size attainable is clearly limited. The difficulties associated with creating short wavelength lasers and high numerical apertures serve to compound this problem. The second issue is that all of the material the beam passes through will be exposed. High resolution can therefore only be reached when the substrate is approximately 2D, meaning structures must be built up by thin layers which both slows the process and makes more complex devices impossible.

In order to improve this method we look toward two (or more) photon interference. When considering a substrate which reacts when exposed to a single photon of energy $E = \frac{hc}{\lambda}$ it is clear that two interacting photons of energy $E = \frac{hc}{2\lambda}$ will induce the same transitions (Figure 1) by simultaneous absorption [10]. In this case the effective wavelength of light being absorbed by the material is in fact λ/N, where N is the number of photons involved in the process. Applying this to equation 1 yields:

$$\omega_0 = \frac{\lambda}{\sqrt{N} \cdot \pi \cdot NA} \quad (2)$$

Where the $1/\sqrt{N}$ dependence comes from the fact that multiphoton absorption is proportional to I^N . We now see that the new effective waist has become inversely proportional to the number of photons required for the transition, allowing for even higher resolution.

In addition to an improved exposure area a multiphoton reaction contributes an intensity dependence. For two photon reactions the rate of absorbance, $W = \delta I^2$ where I is the incident intensity and δ is the (very small) two photon absorption cross section [10]. Because a Gaussian beam's intensity falls off with distance from the axis this allows the size of the exposed area to be manipulated by decreasing the source laser power. The intensity itself is also proportional to the

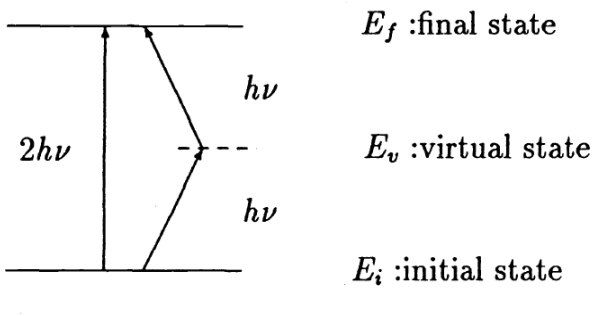

Figure 1 [10]: Energy level diagram for one and two photon absorption processes. Here ν is the frequency c/λ.

cross sectional area of the beam. This second quadratic dependence significantly reduces the probability of photon interactions other than at the beam's highest intensity point, i.e. the focus. Combining these effects means that when using two or more photons for transitions only the small volume at the waist will be affected, as demonstrated with fluorescent dye in Figure 2. The volume for which two photon absorption takes place can be approximated by a cylinder with diameter $d = 2\omega_0$ and height/confocal parameter $b = \frac{d}{NA}$. This volume is often referred to as a voxel (volume pixel).

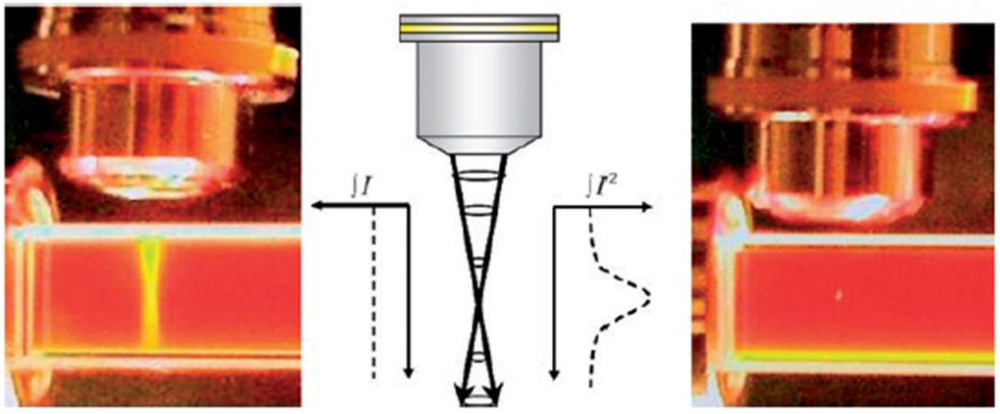

Figure 2 [11]: The region activated by a focused direct write laser. On the left fluorescent dye molecules are driven by a laser whose wavelength allows a single photon to excite the exposure chemistry. The right uses the same sample but longer wavelength light requiring two photons.

It is the combination of high resolution and a small, easily manipulated exposure element which makes this technique so desirable. To reach the high intensities needed for two photon absorption femtosecond lasers are generally used. By either adjusting the samples position with fine stage adjustments or the focus position with a galvanometer the exposed region can be quickly and consistently moved within the sample. Figure 3 shows an example of just how finely detailed and intricate structures using this technique can be made. Our goal is to push DWMP with the positive resist PMMA into the same territory of resolution and complexity currently being achieved with negative resists.

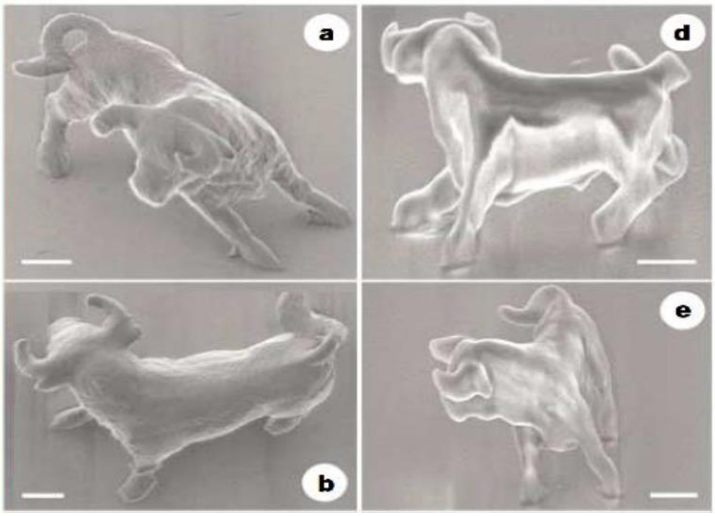

Figure 3 [12]: Bull sculpture in negative resist. This bull, about the size of a red blood cell, is one of the better known sculptures produces using DWMP. The scale bar is 2 um.

Methodology

All DWMP experiments are setup and conducted with a setup as shown in Figures 4 and 5 in the Femtosecond Solid Dynamics (FSD) laboratory of Dr. Enam Chowdhury. All optical components are fixed to an optical table for easy adjustment and stability. The source laser is first sent through a 5x telescope to widen the beam from approximately 5 mm to 2.5 cm. In order to take full advantage of the high NA objective the laser should overfill the back aperture; this both

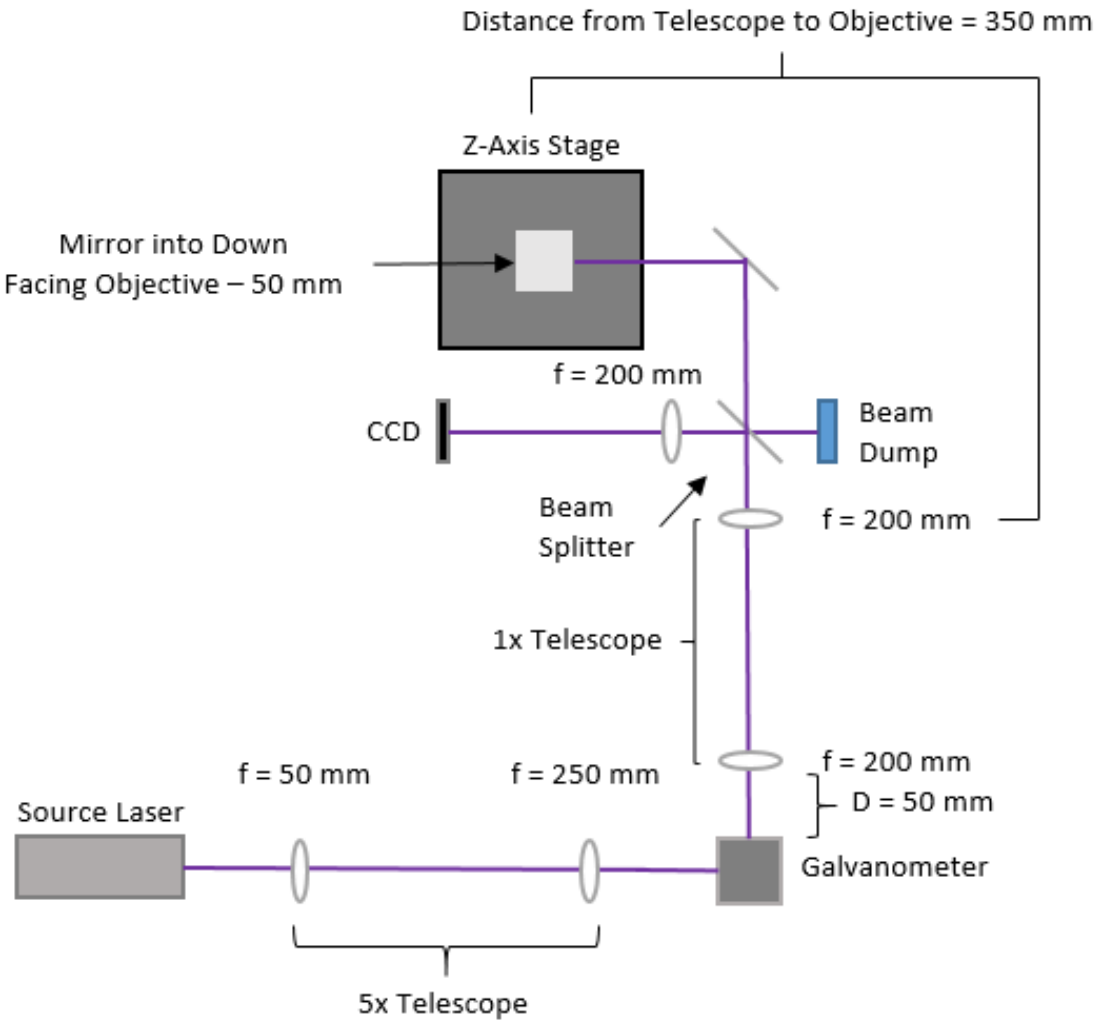

Figure 4: Diagram of the DWMP system.

makes the cross sectional intensity more even and ensures the edges of the beam are well defined near the focus. After expansion the beam is sent through the galvanometer system and a 1x telescope. The 1x telescope is used to shift the conjugate point of the objective nearer to the galvanometer, increasing the range which can be scanned. The beam then passes through a glass beam splitter which deflects some of the returning light from the sample into a camera to be imaged. After the splitter the laser is directed into the objective where it can be focused onto the stage holding the sample.

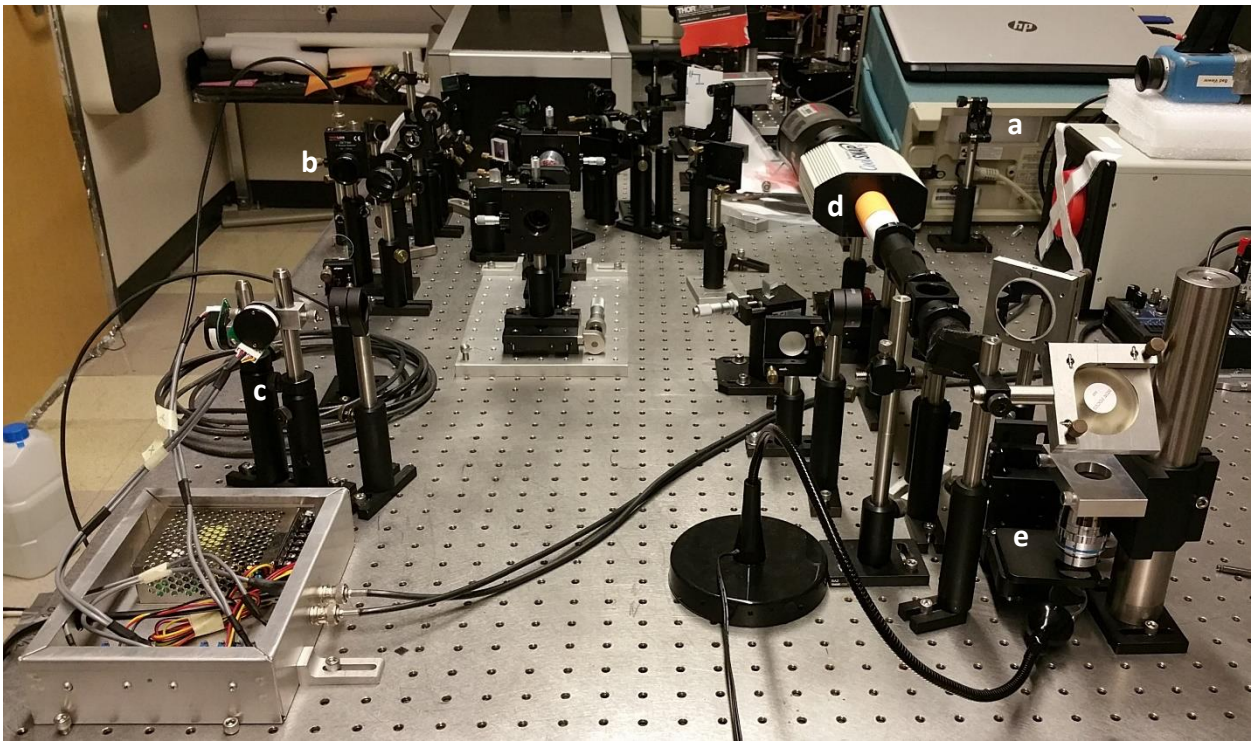

Figure 5: Photograph of the DWMP system in the FSD lab. a) is the birefringent crystal and entryway for the laser beam (on a separate table), b) is a photodiode used to measure the laser power while testing, c) is the galvanometer system, d) is the camera, and e) is the objective lens and stage.

The laser used for our experiment is a homemade ultra-fast (femtosecond) Ti:Sapphire laser operating at 500 Hz with 3.5 mJ/pulse and 773 nm center wavelength. Before entering the DWMP system the beam is sent through a BBO (Beta Barium Borate) crystal to undergo frequency doubling, reducing its wavelength to approximately 387 nm. Because of the high output of the laser no advanced optics are needed to induce frequency doubling, only a simple 3x telescope is used to ensure the full beam passes through the core of the crystal. Pulses with length 30 fs and energy up to 20 µJ can reach the objective. PMMA depolymerizes in the deep UV range (200 - 122 nm) so for photocleavage to take place two photon absorption will necessarily occur at around 193 nm.

The camera, a Photometrics CoolSnap ES is used primarily for finding the correct depth on the sample, but is also useful in visually checking if the laser power has been brought beneath the ablation threshold. The camera is also used when finding the calibration constants needed to run the patterning program. For the objective a Nikon 60x planapochromat water immersion lens with a NA of 1.20 is used. This very high NA is necessary when attempting to minimize feature size, as per equation 1 and 2. Finally the galvanometer is a customized set of mirrors which can rotate on axis and are arranged in a twisted periscope configuration to allow control of the laser angle in the x and y directions. The mirrors are rotated by a piezo system which is in turn controlled by the same computer used for imaging. The galvanometers have a linear relationship between applied voltage and angle turned. Because the angles used in patterning are small the deflection of the focus on the sample can also be approximated as having a linear relationship with applied voltage. The maximum range of the galvanometer on the sample is a circle, centered at the focus, with a radius of ~220 μm.

Samples begin as cover glass and are spincoated in a clean room environment. For this experiment MichroChem 495PMMA A4 (4% solids in Anisole) was spincoated to a thickness of ~250 nm and pre baked at 180 C for 60 s on a hot plate. After exposure samples were developed by immersing in a 3:7 solution of DI water/IPA for 30 s. This development solution, as opposed to more traditional solutions using MIBK, was used because it has been shown to improve contrast in the development of small features in electron beam lithography [13].

Experiments are conducted by loading a sample onto the stage and focusing the objective on the surface of the PMMA using visible light. The laser is blocked and unblocked as needed. When it is time to pattern the laser is unblocked and a LabVIEW program is run which translates predefined patterns into galvanometer movement (Figure 6). For the majority of the experiment

thus far writing has been done at 20 µm/s. Speed dependence for resolution was briefly tested but there was no notable difference up to 100um/s speed. After each test the laser is re-blocked, variables are altered as desired, and the focusing region on the sample is moved to a new area.

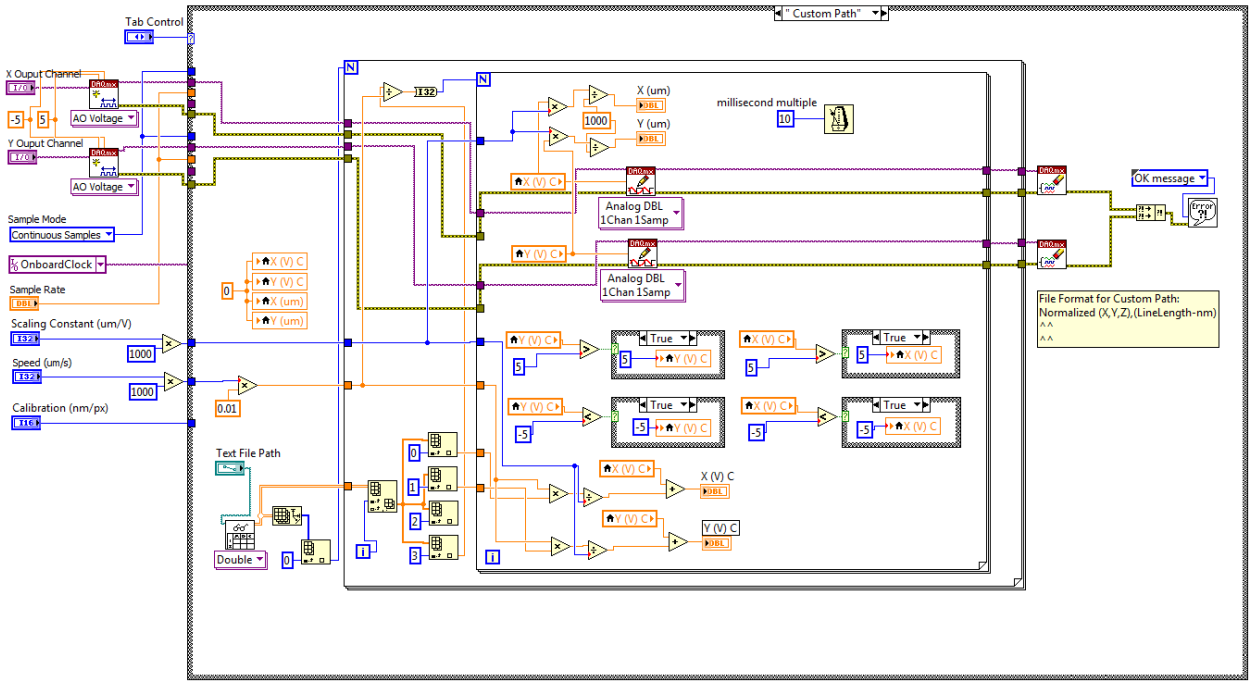

Figure 6: GalvoSystemDrive.VI back panel. This LabVIEW program accomplishes the patterning needs for the experiment. The input is a tab delimited text file with a series of normalized vector magnitudes for the x, y, and z direction and a distance in nm. Depending on the size of the step, simple or complex patterns like spirals, grids, and lettering can be created. The program uses the constants write speed (µm/s), galvanometer calibration (µm/V) and screen calibration (nm/px) to translate these step by step patterns into a smooth (100 iterations/s) voltage stream which guides the galvanometers.

Results

Tests were conducted with powers ranging from 0.13 - 4.78 mW where 1 mW corresponds to 2 µJ/pulse and with write speeds ranging from 20 - 100 µm/s. Power was controlled by directly altering the pump strength and was measured through a calibrated diode before the objective; loss

of energy in the objective, water, and coverslip before reaching the sample has not been taken into account. Write speed was controlled by the galvanometer and computer system. To simplify measurement of the feature size all tests were done with a square wave pattern featuring straight lines of length 50 µm spaced 10 µm apart. As previously mentioned no significant differences in resolution due to write speed arose within that range. Power considerations clearly had the largest effect on feature size and the viability of the process. For tests with power 4.78, 2.60, and 1.25 mW changes in the substrate were visible before chemical processing, implying that either ablation occurred or the material's chemical properties were altered enough to be visible without processing (Figure 7). The most promising results were achieved at 0.50 mW. At this power line widths of 500±50 nm were accomplished, as seen in Figure 8. For tests done at 0.30 mW and 0.13 mW no

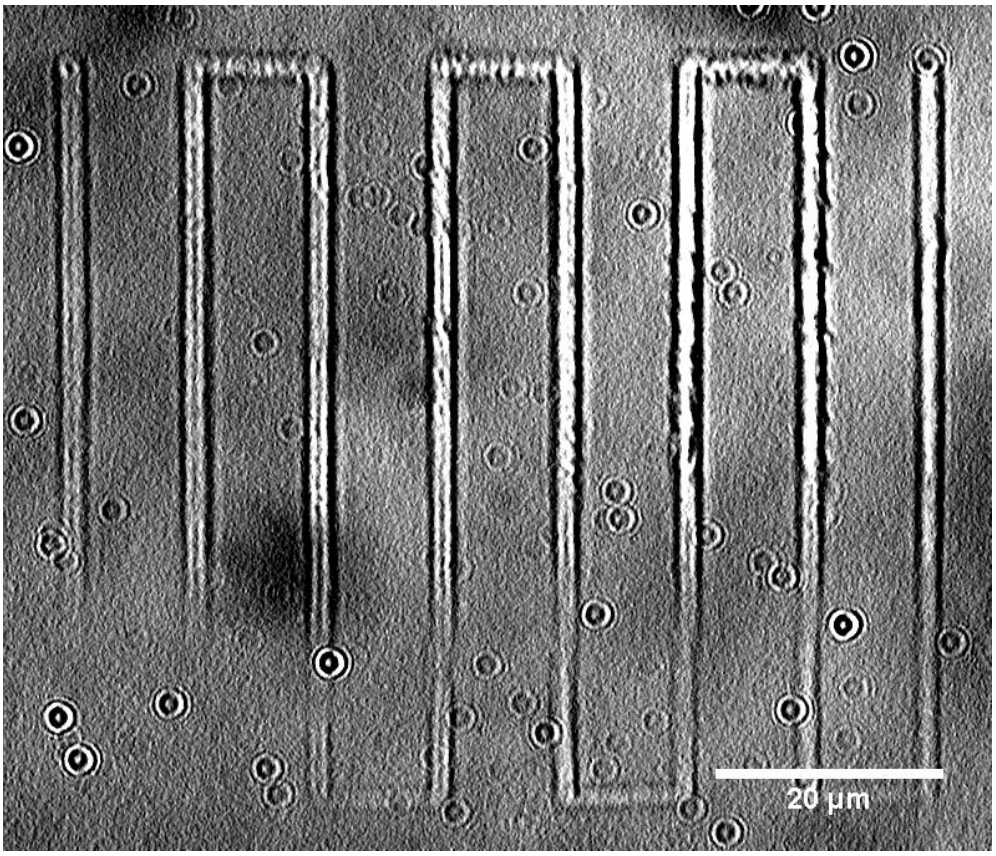

Figure 7: Grid with ablation. The ragged, thick lines produced by scanning the laser at 1.25 mW, which were also visible before development, make it clear that ablation has occurred.

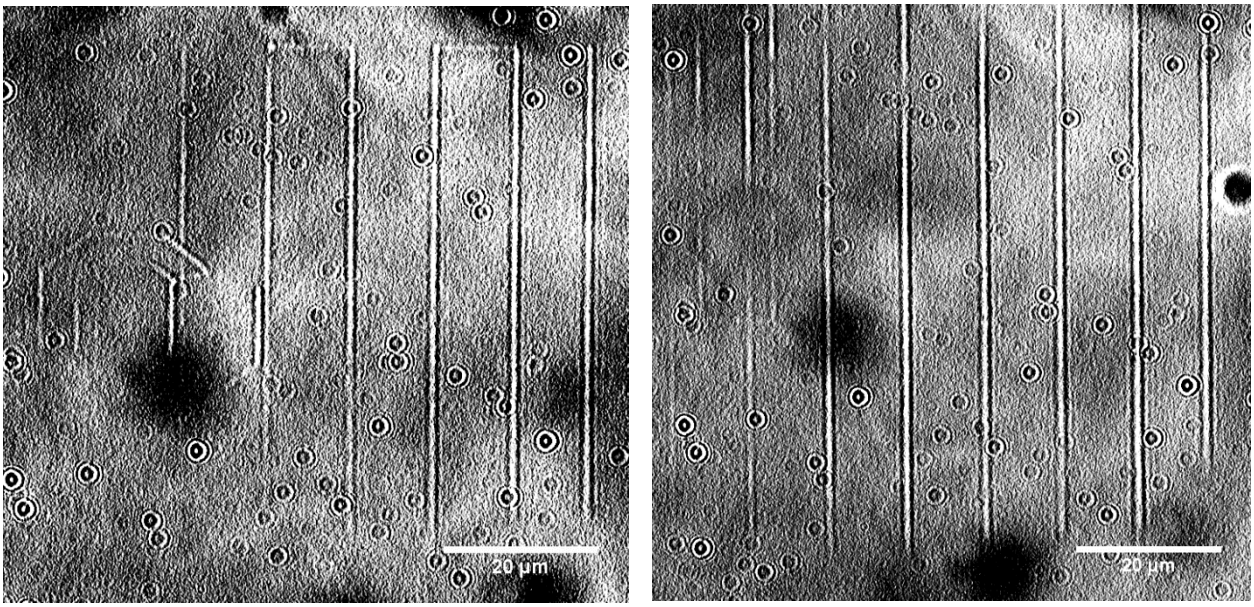

Figure 8: Fine lines in PMMA. These images show lines drawn at 0.50 mW with width 500±50 nm. Both images are proof of the ability to depolymerize PMMA via two photon photocleavage at ~387 nm base wavelength. On the left the top of a slightly out of range "Block O" can be seen. On the right the extended lines trail off at the boundary defined by the galvanometer's range.

patterning was visible with a standard optical microscope, implying that the intensities may not have been significant enough to induce two photon absorption.

Atomic Force Microscopy (AFM) was also used to image the surface of the samples. At 4.78 mW ablation was clearly evident. At 2.60 mW (Figure 9) some grooves could be seen but they did not have consistent width. Patterning done at powers lower than 2.60 mW did not show any surface alteration.

At power 1.25 mW and greater ablation or optical alteration occurs. Our next lowest power tested to date is at 0.50 mW which implies the alteration threshold lies within that range. While finding this threshold is of merit, it is more advantageous to find the power threshold for photocleavage which will represent the power at which voxels are minimized (as a function of power). From the tests so far we can safely assume this lies in the 0.30 - 0.50 mW range.

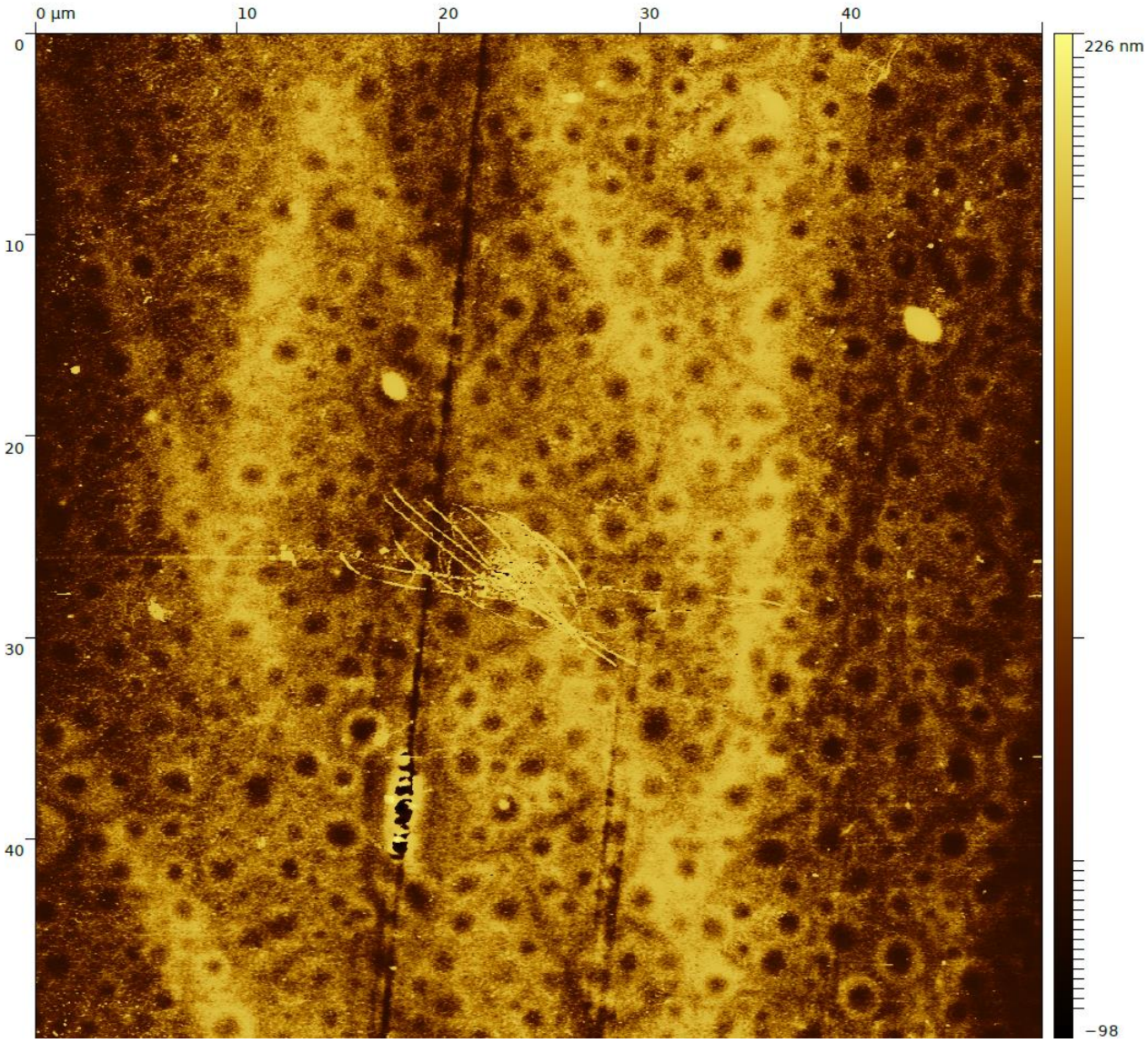

Figure 9: AFM of 2.60 mW sample. This image shows the AFM scan of a grid taken at 2.60 mW. The grooves on the surface made by DWMP vary in width with a minimum size of ~200 nm.

Conclusions

We have succeeded in demonstrating the viability of two photon direct write lithography in PMMA with blue light and achieved a minimum line width of 500±50 nm when examined with traditional microscopy. Furthermore we have defined the power range where the two photon absorption threshold occurs. In future tests this value can be optimized to minimize the feature size even further. A logical next step is to attempt tunnel creation, which will require either

substantially thicker PMMA substrates or PMMA layers imbedded in other non-UV reacting materials. The lack of surface alteration may be a result of the developer, which is milder than those generally used. A more traditional development step may help remove more of the exposed material. Exploration of novel techniques such as using three appropriately polarized interfering beams to create a dark spot (to create toroidal voxels) should also be attempted.

One of the key limitations of this experiment was the difficulty in adjusting power. Because the laser power was adjusted at the pump, before the birefringent crystal, blue light may not have been produced at low power. Frequency doubling is also a nonlinear process, so if the power dips too low the intensity of the red light may exceed that of the blue and give an inaccurate idea of the intensity of light capable of inducing two photon absorption. A method for easily adjusting the power just before the objective, i.e. with filters, would not only improve the accuracy of our results but allow for a finer examination of power dependence on line width. Because of space limitations a non-automated stage capable of movement in the z direction only was used. An x-y stage would allow for finer control of the sample position when imaging and writing, and an automated piezoelectric z stage (controlled by the patterning program) will be necessary for truly 3D microstructures. According to equations 1 and 2 any improvement in the NA of the objective would allow us to create finer features, so an upgrade in that regard would prove useful.

This research represents a first attempt at using DWMP with short wavelength light as a removal process in the positive resist PMMA. The usefulness of developing a method to create complex hollow structures within such a resist is significant, especially to the biological research community. The quick and easy fabrication of novel microfluidic devices in particular would be beneficial to any field which desires to manipulate fluids and cells at the micro and nano scales. The future optimization of DWMP in PMMA will greatly expand the technique's range of viability

and open up new and novel areas of research. The use of devices created by this technique such as NEP can greatly improve the efficiency of drug testing and can potentially speed up the process of finding cures and new insights into cell dynamics. In the long term laboratories may one day incorporate DWMP systems like ours to make fluidic devices as needed. A contained DWMP system using PMMA would serve as a micro scale 3D printer capable of creating hollow structures, cell guides, cell environments, optofluidic devices, and more.

References

1. Gattass, R. & Mazur, E. Femtosecond laser micromachining in transparent materials. *Nature Photonics.* **2,** 219-225 (2008).
2. Baum, A., Scully, P., Basanta, M., Thomas, P., Fielden, P., Goddard, N., Perrie, W. & Chalker, P. Photochemistry of refractive index structures in poly (methyl methacrylate) by femtosecond laser irradiation. *Opt. Lett.* **32**, 190-192 (2007).
3. Jinhai, S., Qiu, J., Zhai, J., Shen, Y. & Hirao, K. Photoinduced permanent gratings inside bulk azodye-doped polymers by the coherent field of a femtosecond laser. *App.Phys. Lett.* **80**, 359-361 (2002).
4. Yamada, K., Ishizuka, T., Watanabe, W. & Itoh, K. Single femtosecond pulse holography using polymethyl methacrylate. *Opt. Exp.* **10,** 1173-1178 (2002).
5. Maruo, S. & Fourkas, J. Recent progress in multiphoton microfabrication. *Laser & Photon. Rev.* **10,** 100-111 (2008).
6. Marder, S., Brédas, J. & Perry, J. Materials for multiphoton 3D microfabrication. *MRS Bulletin.* **32,** 561-565 (2007).
7. Juokazis, S., Mizeikis, V., Seet, K., Miwa, M. & Misawa, H. Two-photon lithography of nanorods in SU-8 photoresist. *Nanotechnology.* **16,** 846-849 (2005).
8. Yamasaki, K., Juodkazis, S., Watanabe, M., Sun, H.-B., Matsuo, S. & Misawa, H. Recording by microexplosion and two-photon reading of three-dimensional optical memory in polymethylmethacrylate films. *App.Phys. Lett.* **76,** 1000 (2000).
9. Higgins, D., Everett, T., Xie, A., Forman, S. & Ito, T. High-resolution direct-write multiphoton photolithography in poly(methylmethacrylate films. *App.Phys. Lett.* **88,** 184101 (2006).

10. Wu, E., Strickler, J., Harrell, W. & Webb, W. Two-photon lithography for microelectronic application. *Proc. SPIE 1674, Optical/Laser Microlithography.* 776-782 (1992).

11. LaFratta, C. N., Fourkas, J. T., Baldacchini, T. & Farrer, R. a. Multiphoton fabrication. *Angew. Chem. Int. Ed. Engl.* **46,** 6238–58 (2007).

12. Kawata, S., Sun, H. B., Tanaka, T. & Takada, K. Finer features for functional microdevices. *Nature.* **412,** 697–698 (2001).

13. Yasin, S., Hasko, D. G. & Ahmed, H. Comparison of MIBK/IPA and water/IPA as PMMA developers for electron beam nanolithography. *Microelectronic Engineering.* **61-62,** 745-753 (2002).