Implementation of Two-Photon Lithography for Fabrication of Three-Dimensional Metamaterials

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BRIEF. We implemented a lithography system that can fabricate patterns in a photoresist using two-photon absorption.

ABSTRACT. The rapidly advancing field of metamaterials is focused on developing materials that have unique optical properties that cannot be found in nature. The materials are fabricated using unit cells with a specific size and shape and are used to manipulate light waves. There are several lithographic techniques for fabricating these materials but most of them only allow for two-dimensional structures. Over the past decade, a new technique called two-photon lithography has emerged that allows for three-dimensional patterning of these and other nanoscale materials. In this process, two-photon absorption occurs at a laser's focal point to create a chemical change in a photoresist. In order to implement the process of two-photon lithography, programs were created using MATLAB and LabVIEW that could pattern structures through manipulation of a piezoelectric-stage and optical shutter. The geometry and size of the structures gives insight on how to improve the two-photon lithography system for future use in the lab. Preliminary structures were created that demonstrate the two-dimensional patterning capability of the system.

INTRODUCTION.

Light is made up of electromagnetic waves that consist of oscillating electric and magnetic fields. When these waves come into contact with materials they are reflected, absorbed, or transmitted through. These interactions are determined by the index of refraction, which is based on two properties, the permittivity and permeability of the material. The permittivity and permeability convey the interactions of the electrical and magnetic field with the material, respectively.

The field of metamaterials is concerned with synthetic materials that have indices of refraction that are not found naturally. Metamaterials are comprised of unit cell structures that are designed to be smaller than the wavelength of light. The physical size, shape, and arrangement of these unit cells allows for manipulation of the permittivity and permeability of the material. Metamaterials are capable of possessing indices of refraction that are negative [1, 2] or even equal to zero and they have a variety of applications, including super lenses, enhanced antennae, and optical cloaking [3].

There are several different types of lithographic techniques that are typically used for metamaterial fabrication. Electron beam lithography is the technique that is most widely used due to its accuracy and precision in fabrication, but this technique and most other techniques only allow for two-dimensional structure patterning. Two-photon lithography is a technique that has emerged within the last decade and it allows for three-dimensional fabrication of these structures. As in other lithographic techniques, two-photon lithography results in the exposure of a photoresist; however, in two-photon lithography a tightly focused laser is used to scan the pattern. At the laser's focal point, two-photon absorption occurs and the chemical state of the photoresist is changed. A piezoelectric-stage that controls the x, y, and z position of the sample is used to determine the pattern in which the focused laser exposes the photoresist. Once a pattern is made, a material of interest can then be deposited into the exposed pattern to form a structure [4, 5].

Two-photon lithography is becoming a significant part of metamaterial research because it allows for the manipulation of the x and y as well as z-direction of a structure. It allows for improved symmetry, precision, and surface smoothness in patterning. This technique can also be used for a variety of applications other than metamaterials, including the polymerization of resin to form structures or the creation of complex biological structures using biomaterials [4].

The goals of this study were to implement a two-photon lithography system and to quantify the precision and accuracy of this process with the application of creating metamaterials. Two specific parameters in this system were targeted for optimization: step size, which is the distance between points in a pattern, and dwell time, which is the amount of time that the laser is focused at a certain point in the pattern. These values can be used to improve precision and accuracy of the resist patterning with the ultimate goal of using the system for metamaterial fabrication.

MATERIALS AND METHODS.

Sample Preparation.

A negative photoresist, SU-8 2000.5 [3, 6], was spun at a thickness of 500 nm on the surface of a clean glass substrate. The photoresist was baked onto the substrate at a temperature of 95° C. An ultra-fast titanium-sapphire laser was then tuned to a wavelength of 750 nm and focused onto the photoresist film. A piezoelectric-stage was used to direct the substrate in a specified pattern about the focal point of the laser. The photoresist was then developed and the laser-exposed photoresist pattern remained on the substrate surface. The unexposed photoresist was removed using SU-8 developer.

Microscope Setup.

In order to focus the laser onto the photoresist film, the beam of the laser had to be aligned as indicated in the layout in Figure 1. The beam was aligned with standard apertures and mirrors that directed it onto the microscope stage. Before the beam reached the microscope, it traveled through a spatial filter and beam expander. The spatial filter removed the lower intensity edge of the raw beam and the beam expander increased the size of the beam spot. The refined and expanded beam was then directed into a 63X oil immersion objective with a high numerical aperture. This focused the beam down to a small and uniform spot on the sample. With the use of these techniques, the laser was focused precisely on the substrate surface.

To determine how well the beam spot was focused onto the substrate surface, a camera, and a photodetector were used. The camera received the microscope view of the sample surface and projected it to a larger computer screen. The camera aided in locating the beam spot on the sample as well as examining the quality of the beam and the angle at which the beam was travelling through the substrate surface.

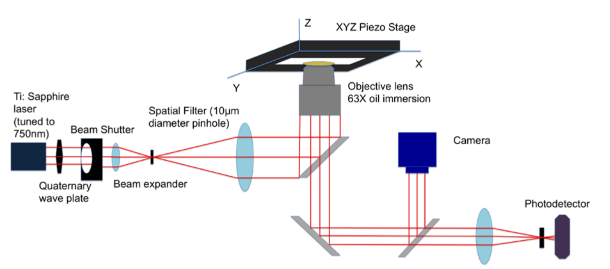

Figure 1. Two-photon lithography system layout: This layout shows the path of the beam as it travels from the laser, through the microscope to expose a sample, and into the camera and photodetector.

The camera was an important device for alignment and it was used to focus the laser for the fabrication of the first pattern, but it didn't serve for determining the precise focal position in the *z*-direction. In an attempt to better gauge the *z*-position of the focal spot, a photodetector [7] was used in place of the camera in the fabrication of the later structures. The photodetector detected the photoresist surface based on a quantitative reading of the reflection from the focal point at the interface of the sample. Specifically, the photodetector signal is maximized when the laser is focused at the interface of the air and the photoresist.

Stage Control.

Programs were created using LabVIEW (National Instruments Corporation, Austin, TX) and MATLAB (The MathWorks, Inc., Natick, MA) that translated and executed patterns into photoresist. The MATLAB program took selected two-dimensional images and converted them into resized binary images. It then created text files containing x and y coordinates of the white pixels in a new binary image based on the size of the image. The LabVIEW program then read the x and y text files as coordinates and directed the piezoelectric-stage to move to those coordinates. The z value of the coordinates had to be entered externally through LabVIEW because the two-dimensional images had no given z value. The LabVIEW program also controlled the step size and a dwell time for the piezoelectric-stage. The step size incremented the distance between points in the pattern and the dwell time determined the amount of time the laser remained at each point in the pattern. These factors determined the accuracy and uniformity of the pattern.

Shutter control was incorporated into this program to prevent exposure in unpatterned areas of the scan. The control function for the shutter opened it at the beginning of a coordinate scan and closed it at the end. After the exposure process was complete, the samples were developed and a 20 nm layer of chromium was deposited on top of the structures. Final samples were then imaged using a scanning electron microscope (SEM).

RESULTS.

Several sets of structures were fabricated using the two-photon lithography process and two of the structure sets are displayed below. For the first structure, the laser was focused based on the camera view of the beam spot size on the sample surface. Once the beam was visually focused as tightly as possible based on the camera image, it was slightly defocused and multiple scans were performed at different z coordinates. The purpose of this was to scan the focal position of the laser through the thickness of the photoresist in order to ensure exposure. The second set of structures was fabricated with the aid of the implemented photodetector, allowing for single layer exposure. This method allowed for more exact determination of z coordinates for exposure of patterns and it ensured that the laser was directly focused within the photoresist.

The template shown in Figure 2b was resized to be a 50 x 50 pixel image. Due to the black border of the binary image in Figure 2b, the image resizing adjusted the white square within the image to be 39 x 39 pixels. These pixels translated to the pattern coordinates and with a step size of 1 μm, the square structure shown in Figure 2a was 39 x 39 μm. This structure (Figure 2a) was exposed with a dwell time of 100 ms and was created using 7 different z-layer scans from the defocused position and the increment in the z-direction between scans was 100 nm.

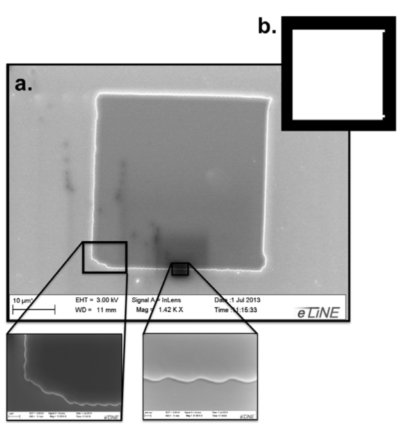

Figure 2. Fabricated square structure: **(a)** SEM image of the fabricated square structure. **(b)** Resized binary image template used to create the different structures in **2a.**

In Figure 2a there are visible inconsistencies in the edges and corners of the structure but the pattern is an accurate portrayal of the binary square image. A consistent ridged pattern can be seen along the bottom of the structure due to the large 1μm step size between points, (lower right inset of Figure 2a). There is visible overexposure throughout, particularly in corners where the structure has been significantly distorted from the original image, (lower left inset of Figure 2a). Overexposure in this structure result from the high dwell time of 100 ms and the numerous z-layers used to scan through the photoresist. The fabricated pattern had a thickness of 500nm, which was the original depth of the photoresist. This structure overall shows little precision and smoothness. These results gave insight on how to refine the patterning for the later structures.

The binary image shown in Figure 3d served as the template for the structures in Figure 3. In these exposures, the photodetector was used to determine the z-position of the photoresist surface, eliminating the need for multiple scans. The image was resized to a 100 x 100 pixel image. With a step size of 250 nm, all three resulting patterns had square dimensions of 25 x 25 μm with a dwell time of 50 ms. All three of the structures were measured to have the same thickness of 500nm, which was the thickness of the SU-8 photoresist used. The first structure, Figure 3a, was scanned at the z-position that was detected to be at the exact surface of the substrate, 500 nm below the photoresist-air interface, at the substrate surface. Figure 3b, the second structure, was scanned at 800 nm below the photoresist-air interface, 300 nm below the supposed substrate surface. The third structure, Figure 3c, was scanned at 1 μm below the photoresist-air interface, 500 nm below the supposed substrate surface. These structures tested the efficacy of the photodetector as a sensor of the photoresist surface position.

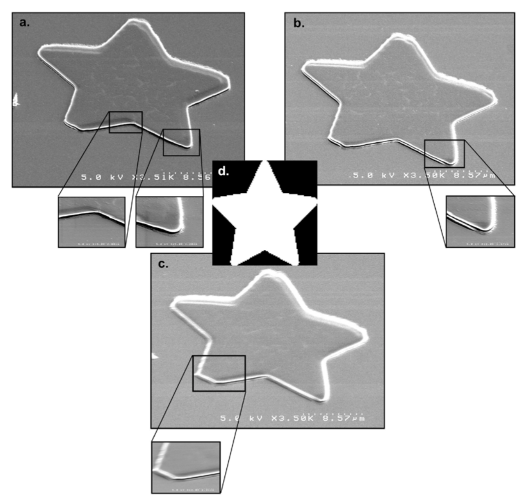

Figure 3. Fabricated Star Structure: **(a)** Tilted SEM image of the first star structure. **(b)** Tilted SEM image of the second star structure. **(c)** Tilted SEM image of the third star structure. **(d)** Resized binary image template that was used to create the star structure in **3a-3c**.

In Figure 3, the edges are generally much clearer than the structure in Figure 2. The lower left inset of Figure 3a shows that there is no longer an issue of ridged edges because there is a smooth angle at the bottom of the star and along the protruding legs. The tilted images here demonstrate the thickness of the structures. The outer insets of the corners are misshapen from a regular star shape, but they resemble the pixelated edges of the original image. The fact that the structures do not exactly follow the pixels of the binary image proves that there is overexposure during fabrication. The structures generally show uniformity, smoothness, and similarity to the template image.

The first structure, Figure 3a, which was fabricated at the theoretical exact surface of the substrate, shows a gap between the substrate surface and the structure. Figure 3b demonstrates this as well, but to a lesser extent. Figure 3c appears to be directly on the photoresist surface. This phenomenon suggests that a scan at a focus of 500 nm below the detected photoresist-air interface does not fabricate the structure directly onto the substrate surface. This is potentially indicative of the fact that the maximum photodetector signal does not exactly correspond to the photoresist surface, an issue that could be due to poor optical alignment of the aperture placed in front of the photodetector.

DISCUSSION.

In this study, a two-photon lithography system was successfully implemented. This technique was determined to be a viable tool in material fabrication. The developed system was tested using a variety of patterned templates. From these tests, two applicable sets of structures were fabricated. The method that was used to most successfully fabricate structures involved focusing the laser inside the photoresist using a photodetector to identify the focal position of the photoresist surface.

The SU-8 2000.5 photoresist used in this study can be exposed by light that is between 350 and 400nm in wavelength. The creation of the structures in this study proves that the two-photon absorption process successfully took place in the photoresist with the laser tuned to the wavelength of 750nm. The type of SU-8 photoresist used was 500 nm in thickness and it was negative tone. It was used because it was able to give clear results as to whether the laser was capable of creating a pattern using two-photon absorption. In the future, structures could be designed in a program such as AutoCAD to better utilize the third dimension. Ultimately, the application of a program that can convert three-dimensional shapes into a readable format would be better for creating three-dimensional structures rather than extruding or offsetting single images.

Factors that influence the smoothness and accuracy of the structures such as step size, dwell time, and resolution were the focus of this study. It was found that a 100 x 100 pixel resolution with a step size of 250 nm created a structure with smooth features, but overexposure could still be a limitation in the accuracy of the system. In the structures of Figure 3, 50 ms was found to be a reasonable dwell time for accurate exposure with a 250 nm step size. The parameters of Figure 3 were more precise than that of the previous structures created in Figure 2 but they can be further refined. More tests could potentially be run to find an optimal value for step size, resolution, and dwell time and create smooth features that more closely resemble the desired pattern. Also in the future, the accuracy of the system could be judged using quantitative tests that determine factors such as the percent of error or the percent of area or volume that matches the initial binary template.

In this system there was initially some difficulty in fabricating structures directly into the photoresist film. This was largely due to problems in determining the focal position and correct laser alignment. The original method of focus involved using the camera to visually focus the laser onto the substrate surface and then scanning the focal position of the laser through the thickness of the entire photoresist in order to ensure exposure. Due to this method's lack of precision, the photodetector method was implemented for the fabrication of the structures in Figure 3 and its success proved it to be a useful tool in laser focus. The application of a pinhole to the photodetector made the device sensitive enough so that it gave a reasonably accurate reading of the sample surface location, though better optical alignment is needed to perfect this system. Even with height inaccuracies, the photodetector method was found to be much more precise than performing multiple scans in the *z*-direction.

Two-photon lithography has been implemented for use in multiple previous studies [4, 5, 7] but it has been observed and refined through the system created in this study. The created shapes cannot determine whether the two-photon lithography technique could be used for more complex designs in the future; however, it does prove that it is a practical method for two-dimensional fabrication and with some optimization, could be applied to fabricate metamaterials for more freedom in manipulation of structure geometry and possibly the realization of metamaterials with novel optical properties. It could contribute to advances of current applications in the metamaterial field such as super lenses, antennae, and optical cloaks but because of its flexibility in patterning the third dimension it could also lead to many new and undiscovered innovations.

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