Simulation and Correction of Angular Defects in Two-Photon Lithography

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In two-photon lithography a high repetition rate laser scans through calculated trajectories in order to induce polymerization in the resin which give rise to complex microstructures. When there are sharp angles within trajectories, the polymerized resin at angles receives more energy from the laser. The polymerized structure becomes larger, and the produced shape gets over-exposure defects. Here we have modeled over exposure defects using numerical simulations and suggested an analytical expression to calculate the correcting coefficients for adjusting laser power. We have demonstrated over exposure defect of free angular structures using this laser power correction.

**Keyword:** Two-photon polymerization, Laser correction method, Angular defect

1. Introduction

Two-photon lithography is a convenient technique to fabricate complex three-dimensional (3D) objects with the sub-micron resolution [1-4]. A voxel is the basic element which is polymerized by focusing the laser beam on a resin at a single position. As the laser beam follows a calculated trajectory, a chain of voxels is polymerized to form a wire. To save time, only the surfaces of micro-objects are fabricated by contour scanning methods [5]. Solid objects are obtained by a further exposure to UV light of the resin which is unpolymerized inside the shells. It is necessary to make all voxels overlap each other during the fabrication for holding the unpolymerized resin inside the closed shells.

During 3D microfabrication, single dimensional slicing method is proposed to obtain laser trajectories from the data of the designed CAD model [6-8]. The CAD model is sliced along one direction into many layers to generate the scanning paths, and then the laser scans these paths to fabricate the micro-object. The quality of the surfaces with gentle slopes is improved by using ultrathin layers. Recently, we have developed the two-dimensional slicing method with a global 3D hatching process to reduce the fabrication time [9]. The global 3D hatching process is applied to generate laser paths of the surfaces with gentle slopes instead of producing more layers. A spiral hatching pattern has been demonstrated to generate continuous trajectories [10]. The continuous scanning path makes the fabricating process smooth without shaking.

Several fabricating strategies have been proposed to address the fabrication quality of micro-objects [8, 11-14]. A multipath scanning method has been proposed to generate two or more layers to enhance the shell thickness. The large thickness can preserve the shape of micro-objects during washing process. A contour offset algorithm has been exercised to correct the
profile inflation due to the size of the voxels on the outer contour. The voxel positions are rearranged to obtain more accuracy profiles. A shape pre-compensation technique has been demonstrated to solve the shrink problem of TPP polymer. The shrinkage rate is taken into the designed model to compensate the anticipated shape and size of the product.

In this work, we investigate the problem and its solution of angular defects during a micro-object fabricated with angular trajectories by using two-photon lithography. When a laser follows a trajectory with a sharp angle to polymerize resin, a non-homogeneous defect is found at the angle due to the laser over-exposure. A series of samples with various angles is fabricated to measure and characterize the collocation of defects and the fabricated angles. Then the energy distributions of the laser exposure are simulated to compare the both trends of the actual defect and the simulated exposure energy. After understanding the relationship between the physical defect and the exposure energy, we derive a laser correction formula to solve the problem of the over-exposure. Finally, the high resolution topography of the modified result can be demonstrated with the use of atomic force microscopy (AFM).

2. **Over-exposure Defect**

Two-photon lithography process with 3D Microfabrication Module (Teem Photonics Inc.) is based on a frequency doubled Nd:YAG micro-laser with 12 kHz repetition rate, 532 nm wavelength, and 0.5 ns pulse width. The module is coupled to an inverted microscope Zeiss Axiovert 200 with microscope objective Aplan x100 NA=1.3 [15,16]. The laser waist $\bar{E}_0$ is 0.23 µm, and the Rayleigh range $Z_R$ is 0.44 µm. Commercial resin (Photomer 3015, Henkel Inc.) is sensitized with 3% two-photon photoinitiator N, N'-bis-(p-methoxyphenyl)-N, N'-diphenyl-4, 4'-diaminobiphenyl. The resin is mounted on a 3D piezoelectric stage (PI nanoprobe P-611.35) with a 1 nm resolution and a working distance of 100 µm. The average laser power employed for fabrication is 20 µW at an exposure time of 10 ms. The lateral and longitudinal sizes of the polymerized voxel are about 0.3 µm and 1 µm, respectively.

The samples, as shown in Figure 1(a), are prepared with the length of 3 µm and a set of different angles $\theta$, 15°, 30°, and 45°. They are fabricated with the voxel distance $d_l$ of 0.12 µm which makes voxels overlap each other. Figure 2(a) and 2(b) display the AFM topography and the height profiles of the samples with the angles of 30° and 45°, respectively. The height profiles show that the over-exposure defect is more significant at an angle of 30° than at an angle of 45°. Figure 2(c) shows the measurements of exceeding heights at various angles. The height of defects is higher at the smaller angles. The exceeding height at the angle of 45° is 143 nm.

3. **Numerical Simulation**

The angular defect results from the over-exposure when the laser trajectory fabricates sharp angles. At sharp angles, the voxel overlapping is larger. It leads to an additional deposition of laser energy, and consequently to an excess of polymerization. In the following, we study how the spatial distribution of the exposure energy changes at angles. The spatial intensity distribution of the

![Figure 1](image1.png)

![Figure 2](image2.png)
l_1 (x, y, z) = \frac{I_0}{1 + \left(\frac{(z - z_i)^2}{Z_k} \right)^2} e^{-2 \left(\frac{(x - x_i)^2 + (y - y_i)^2}{d_i} \right)} \tag{1}

Here, I_0 is the maximum intensity, i is the voxel index, and x_i, y_i, and z_i are the coordinates of its center. The exposure energy is proportional to the product of the exposure time and the square of the laser intensity \cite{12}. Since a polymerized structure is composed of the fabricated voxels, we merge the voxels’ exposure energies into the spatial energy distribution which can be expressed as:

\[ E(x, y, z) \propto \sum_{i=1}^{N} t I_0^2 (x, y, z), i = 1, 2, 3, ... \tag{2} \]

where N is the total number of the fabricated voxels, and t is the exposure time to fabricate each voxel.

The two-photon induced polymerization occurs while the exposure energy is above the threshold energy. For a non-diffusion model, the surface of polymerized shapes can be defined by the location where the exposure energy is equal to the threshold energy. Numerical simulations are carried out with the same parameters of the fabrication. The polymerized shapes and the height profiles along one side of the angles, 30° and 45°, are simulated and shown in Figure 2(d) and 2(e), respectively. Figure 2(c) shows the exceeding heights of the simulation at various angles and the measured results. Figure 2 shows the similarity between the AFM measurement and the shape simulation. Therefore, the spatial energy model of Eq. (2) can be applied to describe over-exposure defects. Moreover, Eq. (2) shows two feasible strategies: adjusting laser power or changing exposure time for our purpose. We choose the way of adjusting laser power because it is practical to operate with the acousto-optic modulator in our equipment and can keep the fabricating speed constant.

We demonstrate a 2D model which is derived from the 3D exposure energy distribution of Eq. (2). The 2D model is based on the calculation of the exposure energy distribution in the plane of z=0. Figure 3 shows that the exposure energy distributions, which is in the plane of z=0, and the full value of the spatial exposure energy have almost the same shape scaled by a constant of 10. Hence, the 2D model will be applied for the laser power correction.
4. Laser Correcting Method

The formula of the laser power correction can be derived from comparing the energy in the line region with that in the defect region shown in Figure 3. To make the description clearer, we number the voxels in the scaling figures shown in Figure 1(b) and 1(c). Due to the Gaussian beam characteristic, we only consider the exposure energy of one voxel and the contributions from its two neighbor voxels during computing the energy of the fabricated line with a constant laser power and a voxel distance \(d_l = 0.12 \mu m\). Hence, an approximate value \(E_i\) of the center energy density of the voxel, numbered as \(i\) in Figure 1(b), is proposed for representing the energy in the line region. \(E_i\) can be expressed as:

\[
cE_i = I_0^2 t + 2I_0^2 t e^{-4d_i^2/\sigma_0^2} + I_0^2 t e^{-45.1^2/\sigma_0^2}
\]

(3)

where \(c\) is a fitting parameter to derive Eq. (3) from Eq. (2). The first term is the energy to form the voxel \(i\), and the second term is the contribution from the two neighbors.

Then, it is also required to find out the value of the over-exposure energy in the defect region. However, the peak value of the over-exposure energy is difficult to be expressed as an analytical equation. Although Figure 3 shows that the energy distribution. In the following, we demonstrate an approximate with analytical expression of the exposure energy for each voxel at angles, and thus the over-exposure energy can be eliminated by correcting the laser power of each voxel at angles. When a sharp angle is fabricated, a voxel on one side is probably influenced by the exposure of the voxels on the opposite side, especially for the opposite voxel which has the same distance from the angle and is generally the nearest voxel. In Figure 1(c), an approximate value \(E_j\) of the voxel energy, which is numbered as \(j\), can be expressed as:

\[
cE_j = I_0^2 t + 2I_0^2 t e^{-4d_j^2/\sigma_0^2} + I_0^2 t e^{-45.1^2/\sigma_0^2}
\]

(4)

Here \(S_{jj}\) is the distance between the two \(j\)-th voxels of the two sides and it value depends on the voxel distance and the fabricated angle. Here the first two terms are explained in Eq. (3), and the last term is the contribution from the opposite voxel. Compared to Eq. (3), the exposure energy of the voxel at angles is greater, and the exceeding amount depends on the distance \(S_{jj}\).

To remove the redundant energy, the two laser powers of generating a voxel and its opposite one at angles should be adjusted together with a correcting value \(z_j\). Thus the exposure energy with correcting laser power can be:

\[
cE_{j,cor} = \beta_j^2 I_0^2 t + 2I_0^2 t e^{-4d_j^2/\sigma_0^2} + \beta_j^2 I_0^2 t e^{-45.1^2/\sigma_0^2}
\]

(5)

Let Eq. (5) equal to Eq. (3), the simple correcting coefficients \(z_j\) for voxel \(j\) can be found as:

\[
\beta_j = \left[1\left(1 + e^{-45.1^2/\sigma_0^2}\right)\right]^{1/2} \quad j = 1, 2, ..., n
\]

(6)

When the used voxel distance or the fabricated angle is smaller, it is required to consider more energy terms from nearby voxels. Therefore, the generalized form of correcting coefficient \(z_j\) is:

\[
\beta_j = \left\{1 + e^{-45.1^2/\sigma_0^2} - \sum_{k=1}^{n} e^{-45.1^2/\sigma_0^2} \right\}^{1/2} \quad j = 1, 2, ..., n
\]

(7)

where \(n\) is the number of the active voxels, and \(S_{jk}\) is the distance between the two voxels at the different sides.

The formula will be applied to set proper laser power of each voxel at angles, and make the overall exposure become uniform. The fabrication with the angle of \(45^\circ\) is simulated with the laser correcting coefficients, which are 60.9%, 90.6%, 99.4% for the first three voxels. Compared to Figure 2(c), Figure 4(a) shows the uniform shape of the numerical result with the laser correction. Figure 4(b) shows the AFM topography of the two TPP microstructures fabricated with and without the laser power.
correction, and Figure 4(c) displays the height profile along the side line. It shows that the laser power correction proposed in our work can effectively reduce angular defects due to laser over-exposure.

![Image](image_url)

Figure 4. Polymer structures with the angle 45°. (a) the numerical simulation with the laser power correction; (b) AFM topography of the samples with and without the laser correction in the left and right side, respectively; (C) Height profile of the samples (with d = 0.12 µm)

5. Conclusions
The over-exposure defects at angular trajectories are studied in this paper. When the laser scans the designed trajectory with an angle, the resin at the angle would receive more energy and produce defects. To study the phenomenon, a set of samples are fabricated and then measured by AFM, and the numerical simulations of laser exposure energy distribution are also carried out. The results show that both trends of the actual fabrication and the numerical simulation are similar. Therefore, a correcting approach based on the concept of the exposure energy is proposed by the use of adapting laser power. The corrected results present that the defect can be compensated through our approach. It can improve the shape quality of the micro product fabricated by laser trajectories with angles.

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