Improving spatial resolution of two-photon microfabrication by using photoinitiator with high initiating efficiency

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The lateral spatial resolution (LSR) in two-photon induced polymerization was improved to 80 nm by using an anthracene derivative (9,10-bis-pentyloxy-2,7-bis-[2-(4-dimethylamino-phenyl)-vinyl]anthracene (BPDPA)) as a highly sensitive and efficient photoinitiator. Photocurable resin containing 0.18 mol % BPDPA exhibited a low polymerization threshold of 0.64 mW at 800 nm. Theoretical calculations showed that the LSR can be increased by reducing the laser power, indicating that the LSR could be improved using more sensitive initiators in the future. © 2007 American Institute of Physics. [DOI: 10.1063/1.2717532]

Laser stereolithography based on two-photon induced polymerization (TPIP) has been established as a powerful tool for three-dimensional (3D) micro- and nanofabrications. By using a tightly focused laser beam in a photoresist, TPIP occurs only in a tiny volume around the focal point, which allows the fabrication of arbitrary 3D structures by directly writing them with a scanning laser spot.1–3 Kawata et al. have reported a “microbull” fabricated by TPIP, which was a significant breakthrough in TPIP microfabrication.2 Moreover, they achieved an improved lateral spatial resolution (LSR) of 120 nm. One of the trends in this area seems to be focused on improving the resolution. Recently, Takada et al. reported a LSR of around 100 nm by intentionally introducing radical quenchers into a photocurable resin.4 However, the addition of radical quenchers could result in an increase in the TPIP threshold. Is there any other way to improve the LSR of TPIP? It is well known that LSR is mainly influenced by two factors: laser intensity and exposure time. Laser intensity directly restricts the region of two-photon absorption (TPA), where radicals are initially generated. Exposure time influences the number of radicals induced by TPA. On one hand, a low TPIP threshold would reduce the size of the region where radicals are initially generated. On the other hand, short exposure time should decrease the number and diffusion of radicals generated by TPA, resulting in localized polymerization in a tiny region. Therefore, it should be possible to improve the LSR of TPIP by using a highly sensitive initiator which could contribute to low threshold and short exposure time. In this letter, we report experiments using an anthracene derivative with high TPIP sensitivity as the TPIP initiator. We investigated the dependencies of LSR on laser power and linear scan speed. We achieved a LSR of 80 nm by increasing the linear scan speed around the TPIP threshold. Theoretical calculations indicated that LSR could be dramatically improved by decreasing the laser power to less than 0.80 mW.

A laser beam from a mode-locked Ti:sapphire laser system (Tsunami, Spectra-Physics) with a center wavelength of 800 nm, a pulse width of 80 fs, and a repetition rate of 80 MHz was used for all TPIP experiments here. The beam was tightly focused into photoresist on a glass cover slip with an oil-immersion objective lens (60×, numerical aperture=1.42). The photoresist was scanned by the focused beam in two dimensions (x-y) with a computer-controlled motor stage.

The photoinitiator used in this study was 9,10-bis-pentyloxy-2,7-bis-[2-(4-dimethylamino-phenyl)-vinyl]anthracene (BPDPA), and its TPA cross section (δTPA) was 294 GM at 800 nm, obtained by a two-photon fluorescence method.5 A series of photocurable resins was prepared to evaluate the effect of the photoinitiator on TPIP. The photocurable resins were prepared using methacrylic acid (MAA) as a monomer, dipentaerythritol hexaacrylate (DEP-6A; Kyoeisya Inc., Japan) as a cross-linker, and BPDPA as the TPIP initiator. The chemical structures of BPDPA and DEP-6A are shown in Fig. 1. The components of the photocurable resins are summarized in Table I. Resins 1 to 5 (R1–R5) were prepared using 0.01, 0.02, 0.05, 0.09, and 0.18 mol % of BPDPA, respectively. For comparison, benzil, a typical conventional photoinitiator in UV photocurable resins, was used to prepare a benchmark resin R6. The δTPA of benzil is less than 20 GM, according to the work of Schafer et al.6

The lowest average laser power, measured before the objective lens, that can guarantee fabricating a solid line with
a linear scan speed of 10 μm/s was defined as the threshold of TPIP. The thresholds for all resins (R₁–R₅) were 5.06, 2.02, 1.60, 1.01, 0.64, and 6.37 mW, respectively (Table I). These results indicate that BPDPA is a much more sensitive photoinitiator than benzil in TPIP. This is due to two reasons: (a) the dimethylamino group in BPDPA makes the molecules electron rich, and it is thus easy to transfer an electron to acceptors in the two-photon excitation process to activate polymerization;⁵ and (b) the dimethylamino group also acts as a coinitiator in the initiating stage.⁶ The relationship between threshold and concentration of BPDPA indicated that the threshold changed very slowly when the concentration of BPDPA in the resin was higher than 0.18 mol %, as shown in Table I. Therefore, R₅ was selected as the sample for further investigation of improving the LSR.

The two key factors mentioned above, laser power and exposure time, were carefully investigated. Rather than the spot-evaluation method reported by Takada et al., we employed the line scanning method, in which the exposure time could be easily controlled by changing the linear scan speed. Scanning electron microscope (SEM) images of solidified polymer lines in R₅ fabricated by TPIP are shown in Fig. 2. The polymer linewidth, which represents the LSR, was around 850 nm at the threshold of 0.64 mW [Fig. 2(a)], when the linear scan speed was 10 μm/s. Then, the linear scan speed was increased to 30 and 50 μm/s to study the variation of LSR at different laser powers [Figs. 2(b) and 2(c)]. When the linear scan speed was 30 μm/s, a polymer line could not be fabricated at the laser power of 0.64 mW due to the shorter exposure time. At this scan speed, the LSR was improved to 318 nm by using a laser power of 0.80 mW. Finally, the highest LSR achieved in this study was 80 nm at a laser power of 0.80 mW and the linear scan speed of 50 μm/s [Fig. 2(d)]. These results indicate that the threshold power increased with decreasing exposure time and the exposure time of TPIP played an important role in improving the LSR.

The widths of the fabricated polymer lines versus laser power are plotted in Fig. 3 for various linear scan speeds. This figure clearly shows that the LSR was improved when the linear scan speed was increased. On the other hand, the LSR of R₅ was 250 nm at a laser power of 10.11 mW and a linear scan speed of 50 μm/s, which indicates that the higher threshold was disadvantageous for achieving high LSR. Consequently, using a photoinitiator with a high initi-

![BPDPA: Photoinitiator](image)

![DEP-6A: Crosslinker](image)

**FIG. 1.** Molecular structures of compounds used as photoinitiator and crosslinker in the photocurable resins.

![Magnified SEM images of polymer lines fabricated by TPIP at laser powers](image)

**FIG. 2.** (Color online) Scanning electronic microscopy (SEM) images of solidified polymer lines by using different laser powers and linear scan speeds of 10 μm/s (a), 30 μm/s (b), and 50 μm/s (c). (d) Magnified SEM image of the polymer line (80 nm) fabricated by using a laser power of 0.80 mW and a linear scan speed of 50 μm/s.

![Relationship between LSR and laser power at different linear scan speeds](image)

**FIG. 3.** (Color online) Relationship between LSR and laser power at different linear scan speeds based on R₅ and R₆.

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**TABLE I. Components of photocurable resins used in this study.**

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>Monomer (mol %)</th>
<th>Cross-linker (mol %)</th>
<th>Photoinitiator (mol %)</th>
<th>Threshold (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>93.13</td>
<td>6.86</td>
<td>0.01</td>
<td>5.06</td>
</tr>
<tr>
<td>R₂</td>
<td>93.12</td>
<td>6.86</td>
<td>0.02</td>
<td>2.02</td>
</tr>
<tr>
<td>R₃</td>
<td>93.11</td>
<td>6.84</td>
<td>0.05</td>
<td>1.60</td>
</tr>
<tr>
<td>R₄</td>
<td>93.09</td>
<td>6.82</td>
<td>0.09</td>
<td>1.01</td>
</tr>
<tr>
<td>R₅</td>
<td>93.01</td>
<td>6.81</td>
<td>0.18</td>
<td>0.64</td>
</tr>
<tr>
<td>R₆</td>
<td>93.01</td>
<td>6.81</td>
<td>0.18 (Benzil)</td>
<td>6.37</td>
</tr>
</tbody>
</table>

*Thresholds of all resins were determined by using a linear scan speed of 10 μm/s.

*Benzil was used as the photoinitiator in R₆.*

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1. Takada et al. 2. Benzil was used as the photoinitiator in R₆. 3. Benzil was used as the photoinitiator in R₆. 4. Benzil was used as the photoinitiator in R₆. 5. Benzil was used as the photoinitiator in R₆. 6. Benzil was used as the photoinitiator in R₆. 7. Benzil was used as the photoinitiator in R₆. 8. Benzil was used as the photoinitiator in R₆.
ating efficiency should not only reduce the threshold but should also improve spatial resolution, which is a key parameter in micro- and nanoscale 3D fabrications.

In order to investigate the possibility of further improvement of the LSR, we performed the following theoretical calculations based on a simple model which mainly deals with the two-photon excitation process and the radical polymerization process. The concentration of the two-photon excited initiators \( [A_e] \), which lead to the formation of radicals by an energy transfer process, is given by

\[
[A_e] = \Phi \frac{\delta_{TPA}}{2(h\omega)^2} [A] \int_{\text{pulse}} P^2 dt \times N_{\text{pulse}},
\]

where \( \Phi (\sim 4 \times 10^{-3}) \) is the quantum efficiency for radical generation, \( \delta_{TPA} \) is the two-photon absorption cross section, \( [A] \) is the concentration of the initiator, \( I \) is the pulse intensity, \( h\omega \) is the photon energy, and \( N_{\text{pulse}} \) is the number of pulses. The size of the solidified polymer region can be estimated by considering the polymerization reactions, which include dissociation reaction of initiators, propagation reaction, and termination reaction. The degree of polymerization \( (P_n) \) is given by

\[
P_n = \frac{k_p[M]}{k_p(2k_d/k_c)^{1/2}[A_e]^{1/2} + k_{ox}[O_2]},
\]

where \( [M] \) and \( [O_2] \) (\( \sim 2.8 \times 10^{-4} \) mol/l) are the concentrations of monomer and oxygen, respectively, \( f \) is the efficiency of the dissociation of the initiator, and \( k_p \) (\( \sim 10^6 \) mol\(^{-1}\) s\(^{-1}\)), \( k_d \) (\( \sim 10^7 \) mol\(^{-1}\) s\(^{-1}\)), and \( k_{ox} \) (\( \sim 2 \times 10^4 \) mol\(^{-1}\) s\(^{-1}\)) are the reaction rate constants of propagation, termination, dissociation of the initiators, and termination by oxygen, respectively. Thus, \( R \), which is the radius of the sphere occupied by a polymer chain, can be expressed in terms of the degree of polymerization \( P_n \) as

\[
R^2 = \frac{a}{6} P_n b^2,
\]

where \( a \) is a constant related to the number of atoms in the monomer and \( b \) is the length of the C–C bond.\(^\text{12} \) The calculated result was obtained assuming a scan speed of 50 \( \mu\)m/s, as well as the value of \( \delta_{TPA} \) obtained experimentally (294 GM at 800 nm for BPDPA, as shown in Fig. 4). The calculated result was in agreement with the experimental data below a laser power of 2.0 mW. However, the experimental values became larger than the calculated results when the laser power was larger than 2.0 mW. This is attributed to a heating effect at the focus spot in the actual experiment, which might cause self-accelerating polymerization, resulting in deviation from the experimental data. The calculated results clearly indicate that the LSR can be improved with reduced laser power, especially when the laser power is less than 0.8 mW.

In summary, two-photon induced polymerization with an 80 nm lateral spatial resolution was achieved by combining extremely low laser power and fast linear scan speed, when a photoinitiator with high initiating efficiency was used. The photoinitiator with high initiating efficiency resulted in a low polymerization threshold, which is advantageous for improving the lateral spatial resolution. Theoretical calculations showed that the lateral spatial resolution can be increased dramatically with reduced laser power, which indicates that LSR could be improved by using a more sensitive initiator in the future.

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\(^12\)P. J. Flory, Principles of Polymer Chemistry (Cornell University Press, Ithaca, New York, 1953).