

N. FANG
C. SUN
X. ZHANG 

Diffusion-limited photopolymerization in scanning micro-stereolithography

Department of Mechanical and Aerospace Engineering, University of California-Los Angeles, 420 Westwood Plaza, Los Angeles, California 90095-1597, USA

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ABSTRACT The trade-off between process speed and resolution in microstereolithography (μ SL) roots on the diffusion-limited kinetics of photopolymerization. Using a numerical model, we have investigated the influence of diffusion dominant effect under high photon flux. Radical depletion turned out to limit the smallest feature achievable to the order of 10 μ m under high process speed. A solution of pulsed laser curing is proposed in order to realize sub-micron resolution in high speed μ SL process.

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1 Introduction

Microstereolithography (μ SL) provides the designers with a simple approach to converting the computer aided designed (CAD) model into truly 3D microcomponents and devices with complex geometry [1–4]. Using a tight focused scanning laser beam to solidify photopolymer resin in a layer-by-layer manner, μ SL forms micro-devices of arbitrary shape on stacked layers. In contrast to conventional silicon micro-machining process, μ SL is free from constraints on the height of the components. In addition, μ SL draws advantages from its precision, automatic process and capacity to incorporate a broad spectrum of functional materials. This promising prototyping technique will find potential applications in microfluidic systems [5], optical waveguides [6], and 3D photonic band gap structures [7].

For the prototyping of 3D micro-devices, resolution and fabrication speed are two critical factors in μ SL process. The former dominates the smallest feature size and the latter limits the process yield rate. We have recently re-

ported an advanced microstereolithography system with 1–2 μ m resolution using single photon absorption [2]. Figure 1 shows two examples of the fabricated polymeric photonic structures using our scanning μ SL system. A common perception in microlithography is that photo-polymerization ratio is simply a function of the exposure dose, that is, the product of intensity and exposure time. This perception leads to an intuitive conclusion that an optimal process speed can be met by increas-

ing light intensity while maintaining the exposure dose. However, the progression of photopolymerization under laser irradiation is an evolving process from liquid to solid which experiences an intermediate gelatinous state. The characteristic time and length scale of this evolving process will constrain the ultimate resolution at a given process speed.

In this paper we will investigate the fundamental mechanism of the interplay of resolution and process speed in μ SL. First, a simple model is proposed to illustrate the diffusion-limited reaction kinetics of localized photopolymerization. From this model, we will show how radical depletion under high photon flux will determine the trade-off between resolution and fabrication speed in μ SL with a laser source operating in continuous-wave or high repetition rate modes. Finally, we will demonstrate the possibility to realize sub-micron resolution with-

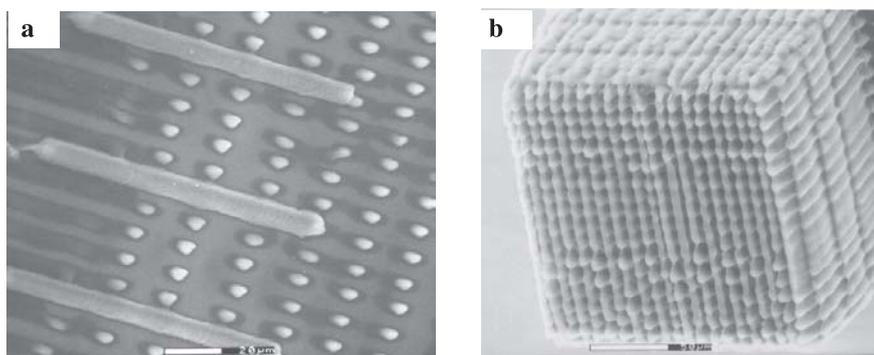


FIGURE 1 The scanning electron micrograph (SEM) of **a** a 2D dot array and line patterns with 10 micron linewidth and 8-by-5 micron dot size and **b** a fabricated 16 layer 3D polymeric photonic crystal by scanning μ SL. In **b** the dots are 3-micron in width with 7-micron spacing and 15-micron in depth. The scale bar in **a** and **b** is 20 and 50 microns, respectively

out sacrificing the process speed in μSL .

2 Numerical model

A schematic of the numerical model is depicted in Fig. 2. The simulation would be carried on a cylindrical volume filled with monomer resin where UV light beam is illuminating the upper surface of the cylinder. The scanning beam is simplified to be stationary with a typical exposure time on the working surface. The incident beam has a distribution of Gaussian profile, namely, $I(r, 0) = I_0 \exp(-2r^2/W^2)$, where I_0 is the peak intensity, and W is defined as beam waist.

The UV curable resin is comprised of monomer, photoinitiator and additives, such as light absorber. In the simulation 1,6-hexanedioldiacrylate(HDDA) monomer with 2% benzoin ethyl ether (BEE) is selected since some fundamental reaction mechanism is intensively studied in this resin from a macroscopic scale down to several microns [2, 8]. The mixture of curable resin has a uniform concentration of components. The total absorption of light in the liquid can be described by Beer–Lambert law, that is,

$$\frac{dI}{dz} = -(\varepsilon[S] + \varepsilon_a[S_a]) I. \quad (1)$$

Here the term $\varepsilon_a[S_a]$ represents the absorption apart from the contribution of the extinction of photoinitiator

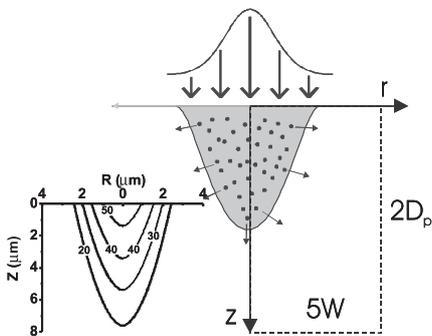


FIGURE 2 A schematic of the numerical model to simulate the photopolymerization in μSL . A Gaussian laser beam is incident to the surface of monomer resin. Photoinitiator molecules, by absorbing the photons, will be split into free radicals (the black particles in the gray region). The inset displays a typical simulated conversion contour of the polymerized voxel under moderate continuous wave illumination ($I_0 = 5.0 \text{ W/cm}^2$, time $t = 0.2 \text{ s}$). The radial definition is 2.7 micron and the depth is 3.4 micron in a threshold of 40% conversion

$\varepsilon[S]$. The total absorption is characterized by a typical penetration depth $L_p = 1/(\varepsilon[S] + \varepsilon_a[S_a])$, and within $2L_p$, the intensity diminishes to about 13% of its value on the surface. Therefore, a volume of $5W$ and $2L_p$ is regarded as an infinite pool outside of the curing region.

The whole UV curing process can be divided into three steps: photoinitiation, propagation and termination. It is recognized that the photochemical reaction in HDDA monomer molecule will release enthalpy [9], thus accompany a heat transfer phenomenon during polymerization. From conservation of internal energy we have

$$\rho C_p \frac{\partial T}{\partial t} = \kappa \nabla^2 T + \frac{d[M]}{dt} \Delta H \quad (2)$$

where ρ , C_p , κ [M] are the density, thermal capacity, thermal conductance and the molar concentration of HDDA monomer, respectively, and ΔH is the total enthalpy released per mole monomer molecules if all of the double bonds are broken during polymerization. The consumption of monomers is governed by the radical propagation kinetics [10] as

$$\frac{d[M]}{dt} = -k_p[R][M], \quad (3)$$

where k_p is the rate constant of propagation reaction, and $[R]$ the corresponding radical concentration.

Due to the Gaussian distribution of laser beam, the non-uniform illumination will establish a concentration gradient of the photoinitiators ($[S]$) as well as radicals in the resin. The gradient will drive the molecules diffusing from

the high concentration region to the low concentration region. Therefore, the mass transfer equations of photoinitiators and radicals can be written as

$$\begin{aligned} \frac{\partial[S]}{\partial t} &= \nabla \cdot (D_{[S]} \nabla[S]) - \frac{1}{2} \varphi \varepsilon[S] I, \quad (4) \\ \frac{\partial[R]}{\partial t} &= \nabla \cdot (D \nabla[R]) + \varphi \varepsilon[S] I - k_t[R]^2, \quad (5) \end{aligned}$$

where φ is the quantum yield of radicals, k_t the termination kinetic reaction rate, $D_{[S]}$ and D is the diffusion coefficient of photoinitiators and radicals, respectively.

It has been noticed in experiments that the polymerization is related to the diffusion of reagent species. However, due to difficulties to determine diffusion effects quantitatively in practice, none of the theoretical models are widely appreciated. Instead, several empirical equations are proposed [11, 12]. In this case, we further assume that the conversion ratio $C (= 1 - \sqrt{[M]/[M]_0})$ for diacrylates) indicates the volume ratio of the solidified part in the computed cell and thus an effective diffusion coefficient $D(C)$ can be determined as a function of conversion ratio:

$$\frac{1}{D(C)} = \frac{(1-C)}{D_l} + \frac{C}{D_s} \quad (6)$$

where D_l and D_s corresponds to the diffusion coefficient in liquid and solid state, respectively. Apparently, it approaches the same limit as $C = 0$ (liquid) and 1 (fully crosslinked solid) as in other empirical relationships.

The parameters necessary to implement the simulation are listed in Table 1. The fourth order of fixed step-size Runge–Kutta integration algorithm

Gaussian Radius	$W = 5 \times 10^{-6} \text{ m}$
Monomer Initial Concentration	$[M]_0 = 4.46 \times 10^3 \text{ mol/m}^3$
Density of HDDA [10]	$\rho = 1.01 \text{ g/m}^3$
Specific Heat of HDDA [10]	$C_p = 1.7 \times 10^3 \text{ J/kg/K}$
Enthalpy [10]	$\Delta H = 1.60 \times 10^5 \text{ J/mol}$
Thermal Conductivity [10]	$\kappa = 0.2 \text{ W/m/K}$
Photoinitiator Initial Concentration	$[S]_0 = 2.23 \times 10^2 \text{ mol/m}^3$
Stabilizer Concentration	$[S_a] = 4.46 \text{ mol/m}^3$
Molar Absorptivity of Photoinitiator [10]	$\varepsilon = 20.0 \text{ m}^2/\text{mol}$
Molar Absorptivity of Stabilizer	$\varepsilon_a = 2000.0 \text{ m}^2/\text{mol}$
Quantum yield for Initiator [10]	$\varphi = 0.1$
Environmental Temperature	$T_0 = 303 \text{ K}$
Radical Diffusion Coefficient [17]	$D = 3.0 \times 10^{-10} \text{ m}^2/\text{s}$
Initiator Diffusion Coefficient [17]	$D_{[S]} = 3.0 \times 10^{-10} \text{ m}^2/\text{s}$
Solid Diffusion coefficient [16]	$D_s = 2.0 \times 10^{-14} \text{ m}^2/\text{s}$

TABLE 1 The computation parameters selected in simulation

was used to solve (1) and (3), while the 2D radical diffusion equation and heat transfer equation are solved by finite control volume method with ADI (Alternating-Direction Implicit) algorithm. The details of boundary conditions, initial conditions and kinetic constants can be found at [13].

3 Results and discussion

3.1 Continuous wave photopolymerization

The simulation was first carried out to model polymerization under exposure of continuous illumination. This simulation gives some interesting physical pictures of polymerization under higher light intensity. Typically the monomer conversion decreases with depth and radial position and increases with exposure time, as shown in Fig. 3a. This results from the highest light intensity at the center of the surface and therefore highest reaction rate. A drop of radical concentration at time $t = 20$ ms is attributed to the acceleration of termination reaction at conversion around 12%, and diffusion effect becomes dominant near this region. After that moment, reaction rate becomes lower so that radical concentra-

tion increases again from the photolyzation of initiators. At a higher monomer conversion, the reaction rate is lower with the maximum conversion approximately at 60%. This is consistent with the results in Fig. 3a.

One may conclude intuitively that with the increase of intensity, polymerization may occur faster and the required processing time can be reduced. On the other hand the simulation result turns out somehow against intuition. Figure 3b illustrates a conversion profile under illumination of high intensity ($I_0 = 5 \times 10^2$ W/cm²) with time $t = 0.1$ s. Surprisingly, polymerization occurs faster in the core of cured region than on the liquid surface where intensity is stronger, as a consequence, the maximum conversion region is located at the core of the final cured part and a “wok” like shape is formed. This phenomenon can be explained by the diffusion dominant effect at high intensity. From parametric analysis, it can be found the consumption of photoinitiator under high intensity is much faster than the compensation rate through diffusion. As a result, the concentration of photoinitiator at surface drops to zero under strong exposure, further conversion is therefore ceased after depletion

of free radicals generated locally. On the other hand, at the core of the curing region light is much attenuated so that it can allow polymerization to proceed until maximum conversion is reached. In this case, very high intensity is not favorable since a larger polymerized part is produced. It indicates the existence of physical limitation in continuous curing since lower intensity means longer curing time and consequently longer diffusion length of radicals.

3.2 Single photon pulsed laser curing

As we described in the introduction, using two-photon polymerization, the resolution of μ SL has recently been increased from several microns to sub-microns [4, 7, 14, 15]. However, an important limitation with this attractive approach arises from the weak sensitivity of commercial UV photopolymers to two-photon excitation. Apart from the complexity of photo-initiator synthesis and high cost of femtosecond laser, the required substantial exposure time and thus a low fabrication speed remains a practical bottleneck for two-photon μ SL. Instead, if the single photon polymerization under pulsed illumination can be optimized to realize sub-micron resolution, it will enable the microstereolithography systems with lower cost light sources, for example a compact, frequency doubled Nd:YAG laser with pulse width to the order of nanosecond [15]. In this section, we set to explore the possibility to utilize this class of pulsed light sources for advancing the fabrication resolution limit in scanning microstereolithography.

Pulsed laser polymerization has already emerged as an analytical method to determine photopolymerization rate parameters [11]. In this method, a short laser pulse is applied to explore the extinction of photoinitiator under high intensity and different time scales are introduced in order to balance diffusion and reaction rate. Here we take a numerical approach to explore the possibility to optimize the fabrication resolution in μ SL using pulsed laser. The variation of normalized photoinitiator concentration and radical concentration at center of liquid surface is depicted as a function of curing time t in Fig. 4a. The dashed rectangular region indicates the pulse duration. It is obvious that more than 50%

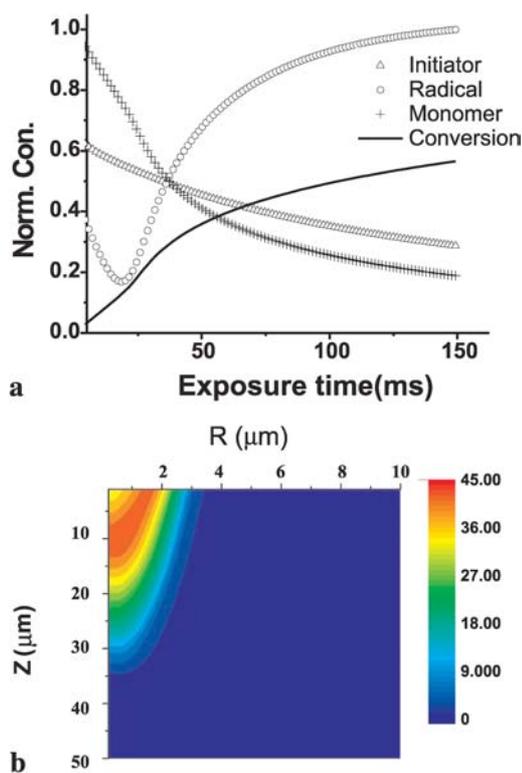


FIGURE 3 a Variation of normalized conversion and concentration at the center of the liquid surface as a function of exposure time. By consumption of monomer and photoinitiator, the conversion ratio increases with exposure time. b Monomer conversion profile under exposure of $I_0 = 5.0 \times 10^2$ W/cm², time $t = 0.1$ s. In this case, the radial definition is 3.8 micron and the depth is 16 micron in a threshold of 40% conversion.

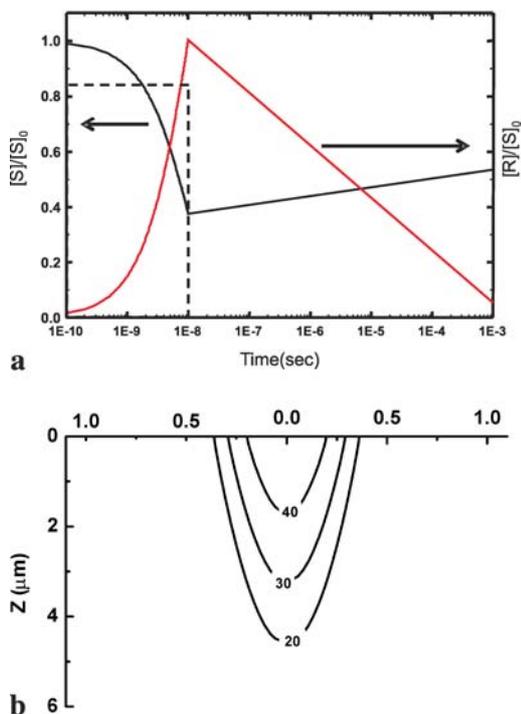


FIGURE 4 a Variation of normalized concentration at center of the liquid surface as a function of exposure time. $I_0 = 10^6$ W/cm², pulse duration 10^{-8} s (the dashed rectangle region), period 2×10^{-3} s. b Monomer conversion profile under exposure of $I_0 = 10^6$ W/cm², pulse duration 10^{-8} s, period 2×10^{-3} s, and total curing time 0.05 s. The radial definition is 0.44 micron and the depth is 1.6 micron with a threshold of 40% conversion

transfer rate through diffusion. By introducing a different time scale to balance these factors, this model predicts that pulsed laser may provide better resolution in μ SL. Further optimization of processing parameters is expected with validation from experiments.

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REFERENCES

- 1 K. Ikuta, K. Hirowatari: Proc. IEEE MEMS'93, 42 (1993)
- 2 X. Zhang, X.N. Jiang, C. Sun: Sens. & Act. A 7, 149 (1999)
- 3 B.H. Cumpston, S. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Heikal, S.M. Kuebler, I.-Y.S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S.R. Marder, J.W. Perry: Nature **398**, 51 (1999)
- 4 S. Kawata, H.-B. Sun, T. Tanaka, K. Takada: Nature **412**, 697 (2001)
- 5 K. Ikuta, T. Ogata, M. Tsubio, S. Kojima: Proc. IEEE, The Ninth Annual International Workshop on MEMS, New York, 301 (1996)
- 6 J. Neumann, K.S. Wiekling, D. Kip: Appl. Opt. **38**, 5418 (1999)
- 7 M. Straub, M. Ventura, M. Gu: Phys. Rev. Lett. **91**, 043901 (2003)
- 8 C. Sun: PhD thesis, Pennsylvania State University, 2002
- 9 G.R. Tryson, A.R. Shultz: J. Polym. Sci. **B17**, 2059 (1979)
- 10 L. Flach, B. Chartoff: Polym. Eng. & Sci., **35**, 483 (1995)
- 11 M. Buback: Makrom. Chem. **191**, 1575 (1990)
- 12 M. Buback, R.G. Gilbert, G.T. Russell, D.J.T. Hill, G. Moad, K.F. O'Driscoll, J. Shen, M.A. Winnik: J. Polym. Sci. A **30**, 851 (1992)
- 13 M. Xi: Masters Thesis, Pennsylvania State University, 2000
- 14 J. Serbin, A. Egbert, A. Ostendorf, B.N. Chichkov, R. Houbertz, G. Domann, J. Schulz, C. Cronauer, L. Frohlich, M. Popall: Opt. Lett. **28**, 301 (2003)
- 15 I. Wang, M. Bouriau, P.L. Baldeck, C. Martineau, C. Andraud: Opt. Lett. **27**, 1348 (2002)
- 16 S.B. Brown, C.M. Orlando: In: *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol.14 (Wiley-Interscience, New York 1988) pp. 169–189
- 17 J. Brandrup, E.H. Immergut: *Polymer Handbook*, 3rd ed. (Wiley, New York 1989)
- 18 A. Reiser: Photoreactive polymers: the science and technology of resists (Wiley, New York 1989)

of photoinitiator is consumed within the duration of first pulse. However, in order to let the photoinitiator to recover back to its original level through diffusion, the characteristic time (L^2/D) is about 10^{-3} s. This again supports our argument about the diffusion dominant effects in the previous section. From this characteristic time, we can estimate that the minimum resolution for the μ SL process is about 1 μ m.

On the other hand, pulsed laser curing provides another opportunity to reduce the total curing time, thus shorten the fabrication cycle. The depletion of photoinitiator during pulse illumination can be compensated by diffusion during the rest of pulse period of 10^{-3} s. Therefore, most of the radicals generated in the center of illumination are applied to reaction and only a small amount of them diffused out. Assuming a tight focusing spot of 0.28 micron with a $NA = 1.3$ objective, the resulted conversion profile is shown in Fig. 4b. The polymerized feature has a minimum radius of 0.44 micron and depth

of 1.6 micron. It agrees with our proposition that matching the balance of reaction and diffusion by introducing different time scale, optimization in resolution can be achieved with the application of pulsed laser curing. Furthermore, the pulsed laser curing draws benefit from both higher conversion ratio within cured volume and reduced curing time and finer cured shape.

4 Conclusions

In summary, the introduction of diffusion terms in this model helps to understand the behavior of polymerization at high intensity. In the original model where diffusion is neglected, no flux of chemical species will be allowed to compensate the loss of photoinitiator at center; therefore the conversion at center of the surface is extremely low, which contradicts the experimental results. By considering the diffusion terms, the physical constraint of photopolymerization is explored and attributed to the competition of photochemical reaction rate and mass