Evanescent light photopolymerization and measurement of cure depth in nanostereolithography

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Nanostereolithography using evanescent light has been proposed as a means to realize submicrometer resolution. In this study, cured polymers of submicrometer thickness have been obtained using an evanescent light exposure apparatus. Examination of the controllability of the cure depth proves that the cure depth can be controlled at a standard deviation of at most 12 nm by configuring the polarization, the exposure energy, and the incident angle. The evanescent light photopolymerization process can be differentiated into two modes in terms of exposure energy per second. These results indicate that nanostereolithography can fabricate three-dimensional structures with submicrometer resolution. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2889451]

Microstereolithography allows the fabrication of complex three-dimensional structures by curing liquid photopolymer.[1] It has been shown that by a layer-by-layer process,[2–4] three-dimensional devices with micrometer resolution can be rapidly fabricated, while a two-photon-absorption process[5–7] has recently improved this method's spatial resolution. However, the former is not able to realize submicrometer resolution and the latter requires an expensive femtosecond laser. In the present study, we intend to establish a microstereolithography method which allows rapid submicrometer fabrication through improvement of the layer-by-layer process. In the conventional layer-by-layer process, since the propagating light, used as the exposure energy, is transmitted through the photopolymer, the cure depth (polymer thickness) exceeds 10 μm, thus, not allowing submicrometer longitudinal resolution. In addition, it is almost impossible to achieve submicrometer lateral resolution because the cure depth is greater than the focal depth of the objective lens of an imaging system. To resolve these issues, we propose a nanostereolithography method[8] that uses evanescent light instead of propagating light as the exposure energy. Evanescent light is partially localized energy at the boundary within the near-field region under total internal reflection;[9] thus, the cure depth would be less than 1 μm. This nanostereolithography method is capable of fabricating large three-dimensional devices rapidly with submicrometer resolution since it is based on the layer-by-layer process which encompasses large areas at a single exposure. Only a few papers[10,11] have reported that evanescent light could polymerize photopolymer, with its application aimed only at lithography employing an elementary prism unit. This letter focuses on evanescent light photopolymerization, in which we verify the evanescent light photopolymerization and measure the cure depth to examine the controllability of the method's longitudinal resolution with a developed apparatus.

In conventional layer-by-layer microstereolithography involving propagating light exposure, cure depth C_d of cured polymer is expressed as follows:[1]

$$C_d = D_p \ln \frac{U}{U_c}, \tag{1}$$

where D_p is the penetration depth (inverse of photopolymer absorption coefficient α), U is the exposure energy, and U_c is the threshold exposure energy. The cure depth of photopolymer KC1162 (Free-radical type, JSR Corp.) utilized in this study has been measured at 44.4 mJ/cm^2.

In nanostereolithography, the cure depth depends on attenuation coefficient of evanescent light β as well as absorption coefficient α. The cure depth is inversely proportional to α plus 2β. Coefficient α is on the order of 10^2 or 10^3 cm^{-1} and coefficient β is on the order of 10^6 cm^{-1}. Hence, the cure depth largely depends on β. Assuming that photopolymer is an isotropic medium, the cure depth in nanostereolithography is formulated as follows:[8]

$$C_d = \frac{\lambda}{4\pi n_2 \sqrt{(n_1/n_2)^2 \sin^2 \theta - 1}} \ln \frac{\tau(\theta)U}{U_c}$$
$$\left[= \frac{1}{2\beta} \ln \frac{\tau(\theta)U}{U_c} \right], \tag{2}$$

where λ is the wavelength of the laser beam, n_1 is the refractive index of glass, n_2 ($<n_1$) is the refractive index of photopolymer, θ is the incident angle, and $\tau(\theta)$ is the constant depending on the polarization and the incident angle.[12] Given that actual values in microstereolithography are assigned to Eqs. (1) and (2), the cure depth under evanescent light exposure would be calculated to be less than 1 μm, whereas the cure depth under propagating light exposure would be calculated to be more than 100 μm.

Figure 1(a) shows the evanescent light exposure apparatus. It consists mainly of a laser source at 488 nm, a resin tank, and a high-power objective lens with a numerical aperture (NA) of 1.65. A collimated light beam passes through a planoconvex lens after the diameter of the beam is changed by means of a variable aperture. The beam is focused after the lens and enters the periphery of the objective pupil. The beam is recollimated at the objective lens and propagates to the cover glass through the immersion oil. When the incident angle is greater than the critical angle, evanescent light is generated on the top surface of the cover glass. Refractive indexes of the objective lens, the immersion oil, and the

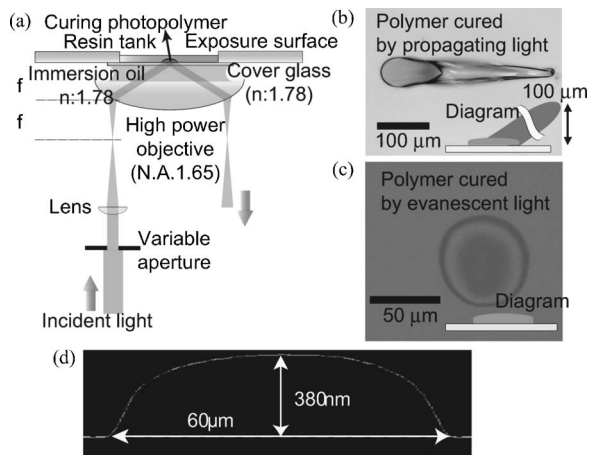[a]Electronic mail: takahashi@nanolab.t.u-tokyo.ac.jp.

FIG. 1. (a) Schematic diagram of an evanescent light exposure apparatus. (b) Polymer cured by propagating light. (c) Polymer cured by evanescent light. (d) Section profile of the polymer cured by evanescent light.

FIG. 2. Semilogarithmic graphs of the cure depth with exposure energy: (a) P-polarization, $P=220$ mW/cm^2, (b) P-polarization, $P=570$ mW/cm^2, (c) S-polarization, $P=460$ mW/cm^2, and (d) S-polarization, $P=610$ mW/cm^2.

cover glass are all 1.78, which form a solid immersion lens.[13] The diameter of the beam is reduced 100 times by the lens and the objective lens. The refractive index of photopolymer is 1.51 so that the critical angle would be 58.0°. A raising unit would be set above the cover glass, which would go up and down during the layer-by-layer process.[14] By installing a tube lens and a charge-coupled device, an optical microscope is configured which allows in-process observation.

Liquid photopolymer placed on the cover glass was exposed to evanescent light. The incident beam was p-polarized, the incident angle was set at 65°, and exposure energy U was set at 2400 mJ/cm^2. The beam diameter was 60 μm at the exposure surface as the aperture diameter was 6 mm. Photopolymer was also exposed to propagating light under the same experimental conditions except for the incident angle (set at 55°). Cleaned with ethanol and diethyl ether, the obtained cured polymers were observed via an optical microscope. Figures 1(b) and 1(c) show optical microscope images of cured polymers produced by propagating and evanescent light, respectively. The polymer cured by propagating light had a long tilted pattern and had a thickness of more than 100 μm. On the other hand, the polymer cured by evanescent light had a thin discoid pattern and had a thickness of less than 1 μm. Figure 1(d) shows a section profile using a white light interferometer (Zygo Corp.) and the thickness was measured at 380 nm. This result demonstrated that evanescent light exposure was sufficient to polymerize liquid photopolymer, with a cure depth expected to be on the submicrometer order.

The polarization, exposure energy per second P, and total exposure energy U (P times exposure time) were then varied and the cure depths of the obtained polymers were measured. The incident angle was set at 65°. Figures 2(a)–2(d) show semilogarithmic graphs of the cure depth in relation to exposure energy. The photopolymerization process was carried out more than three times under the same experimental conditions. Experimental values are plotted on the theoretical line calculated using Eq. (2). A cure depth of 5 nm was achieved with very little exposure energy. Notice that the standard deviation of the cure depth under each condition is less than 10 nm. This result indicates that sufficient controllability can be gained by configuring the polarization and the exposure energy. These graphs also show that the photopolymerization process can be differentiated into two
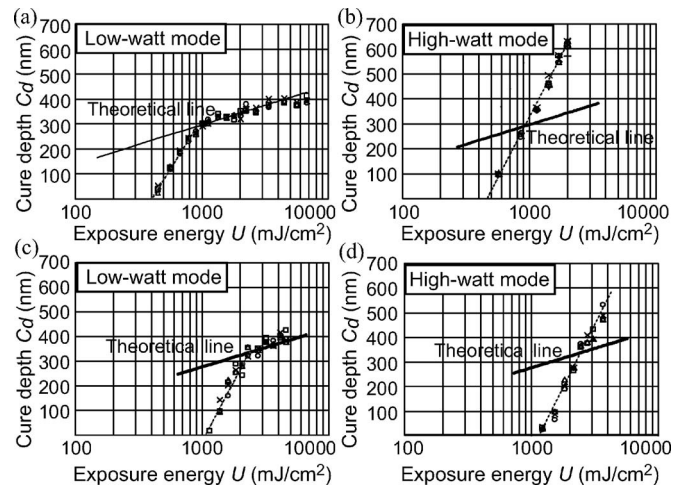
modes in terms of exposure energy per second P. One is defined as a low-watt mode [Figs. 2(a) and 2(c)] and the other is defined as a high-watt mode [Figs. 2(b) and 2(d)]. In the low-watt mode, the gradient ($1/\beta$) is larger than that of the theoretical line in the first section. The gradient would be the same as that of the theoretical line in the latter section. In contrast, the gradient in the high-watt mode is larger than that of the theoretical line as well as the low-watt mode and the gradient in the latter section remains the same. In the high-watt mode, components cured by propagating light exposure appeared in the manner shown in Fig. 1(b) and the cure depth increased to over 10 μm when the exposure energy was more than approximately 5000 mJ/cm^2. In these graphs, the horizontal intercepts indicate threshold exposure energy U_c. Table I lists the gradient in the first section and U_c at each condition. The gradients are considerably larger than the theoretical values. In regards to threshold exposure energies, U_c in a p-polarization condition is about ten times as large as the theoretical value and U_c in s-polarization is about three times as large as the value in p-polarization. This difference between polarizations is not attributed to only $\tau(\theta)$ since $\tau(\theta)$ in s-polarization differs only negligibly from that in p-polarization.

These results may be attributed to dissolved oxygen and polymer lump scattering. In the exposure process, free radicals induced by light energy do not first react with monomers but scavenge dissolved oxygen. The photopolymerization process begins only once monomers are able to compete with oxygen.[15] Since the evanescent light energy is substantially localized, dissolved oxygen at a smaller distance would not be scavenged and it would diffuse to the surface. Thus, the

TABLE I. Gradient and threshold exposure energy.

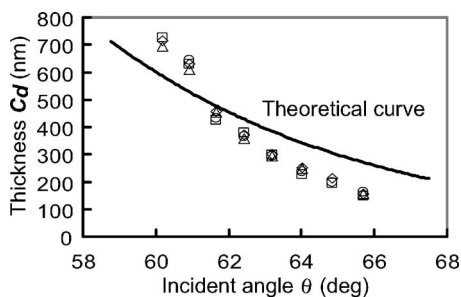| Condition	mode	Gradient ($1/\beta$) (nm)	U_c (mJ/cm^2)
(Theoretical value)		68.4	44.4
P-polarization, 220 mW/cm^2	Low-watt	320	386
P-polarization, 570 mW/cm^2	High-watt	414	459
S-polarization, 460 mW/cm^2	Low-watt	538	1112
S-polarization, 610 mW/cm^2	High-watt	438	1158

FIG. 3. Relation between cure depth and incident angle.

threshold exposure energy becomes larger. Once the photopolymerization process begins, the gradient would be larger since little dissolved oxygen exists near the exposure surface. After most liquid photopolymer near the surface is photopolymerized, the gradient would be the same as the theoretical line in the low-watt mode. Concerning the difference of threshold energies between polarizations, the electric dipole vector in the photopolymer is not directed toward the depth direction in *s*-polarization exposure. Therefore, dissolved oxygen becomes more difficult to scavenge and the threshold would be larger.

As the radical photopolymerization proceeds, a crosslinking reaction occurs to produce entangled polymer lumps. The diameter of a polymer lump can depend on the exposure energy per unit time, just as, in the thermal radical polymerization, excess thermal energies per unit time can induce density inhomogeneity, which makes a polymer lump larger.[16] In the high-watt mode, scattering propagating light energy could polymerize photopolymers. This is because the cured polymer lump size is so large that scattering propagating light energy per unit time could be large enough to provide free radials to scavenge dissolving oxygen per unit time. Thus, similar amounts of incident exposure energies between two modes do not induce the same cure depths and, in the high-watt mode, the components cured by propagating light would occur. Scattering efficiency is proportional to the sixth power of the diameter of the scattering source[17] so that small differences of P could induce two different modes.

The influence of incident angle on cure depth was then examined. Exposure energy per second P was set at 190 mW/cm^2, the exposure time was set at 5 s, and liquid photopolymer was exposed to *p*-polarized evanescent light at various incident angles. Figure 3 shows the relation between cure depth and incident angle. Experimental values are plotted with the theoretical curve. Cured polymers have thicknesses ranging from 150 to 700 nm. The standard deviation of the thickness at each angle is less than 12 nm, which indicates sufficient controllability by configuring the incident angle. When the angle is over 61°, the cure depth is less than the theoretical value, whereas the cure depth exceeds the theoretical value when the angle is less than 61°. In this

experiment, since P is set as the low-watt mode, experimental values should be less than the theoretical value. This result stems from the fact that constant $\tau(\theta)$ depends mainly on incident angles. Constant $\tau(\theta)$ increases as the incident angle decreases. Hence, the total exposure energy becomes larger and the cure depth would exceed the theoretical value under the condition of a smaller incident angle.

In summary, a method of nanostereolithography using evanescent light has been proposed and measurement of cure depth have been demonstrated. Cured polymers of submicrometer thickness have been obtained and a cure depth of 5 nm was achieved using very little exposure energy. The controllability of the cure depth has been examined, with the result proving that the cure depth could be controlled at a standard deviation of less than 12 nm by configuring the polarization, the exposure energy, and the incident angle. In addition, the evanescent light photopolymerization process has been differentiated into the low-watt and high-watt modes in terms of exposure energy per second P. These results indicate that nanostereolithography has the ability to fabricate three-dimensional submicrometer structures with a high degree of controllability through integration with the layer-by-layer process.

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