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Submicrometer thickness layer fabrication for layer-by-layer microstereolithography using evanescent light

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ABSTRACT

We propose a novel one-shot layer-by-layer microstereolithography method using evanescent light to achieve submicrometer spatial process resolution. Theoretical and experimental analyses focusing on the vertical process resolution confirm that a layer of submicrometer thickness can be photopolymerized with good thickness controllability (standard deviation of 10 nm) and that the proposed method of using evanescent light is compatible with layer-by-layer stereolithography.

1. Introduction

Microstereolithography is recognized as one of the most important micromanufacturing techniques available today [1]. Especially, with the increasing demand for micro 3D structures manufacturing with a spatial process resolution of submicrometer in various fields such as micro-electro-mechanical, micro-opto-mechanical, and microfluidic systems, and so on, the highest degree of flexibility in micro 3D fabrication of microstereolithography is rapidly gaining in importance [2]. A number of microstereolithography techniques [3,4] have been developed, which can be classified into two main types on the basis of the principle employed: two-photon photopolymerization [5] and layer-by-layer microstereolithography [6–11] (Table 1).

The former type, which relies on the nonlinear process of two-photon absorption, is well known as one of the most effective methods of achieving high three-dimensional spatial process resolutions that are beyond the diffraction limit – down to 100 nm. However, a scanning process of a fine volume of two-photon absorption is inherently a rather time-consuming process and has additional problem that the fabrication time is essentially dependent on the complexity of designed microfeatures.

The latter type can be characterized as an extension of conventional stereolithography methods widely employed in rapid prototyping for relatively macroscopic industrial components such as automobile parts and mobile phone chassis [12–15]. Thus, it stands in contrast to the former type, which is a concept developed solely for microfabrication. Fig. 1 shows one example of a layer-by-layer microstereolithography method [8]. Here, the risk of introducing dynamic fluctuation of the fluid surface, one of the most important factors from the viewpoint of heightening an affinity for micromanufacturing [2], is eliminated by curing the photosensitive resin from the bottom through a glass window.

Like the method shown in Fig. 1, some methods categorized as layer-by-layer methods have the significant advantage of being compatible with one-shot exposure, where a complete layer is polymerized in one exposure using a dynamic mask such as a liquid crystal display (LCD) or a digital micromirror device (DMD) with projection optics to reduce the image size [8–11].

Thus, one-shot layer-by-layer methods can achieve much higher throughput regardless of the complexity of the features. However, the process resolution of such methods does not meet the requirement for next-generation 3D micromanufacturing, where a submicrometer resolution is necessary. Because a freely propagating light of exposure energy is essentially governed by the diffraction limit and at the same time causes a surplus growth in the liquid resin, which makes the improvement of a spatial process resolution beyond 1 μm scale difficult.

In this research, by taking advantage of its practical higher productivity of one-shot layer-by-layer microstereolithography described above, we propose a method of achieving a submicrometer process resolution in three dimensions together with one-shot layer-by-layer exposure: instead of conventional propagating light and far-field optics, we employ near-field evanescent light to localize the light energy for photopolymerization to a small volume, independent of the diffraction limit of freely propagating light. From the viewpoint of an evanescent light application to microfabrication, there are various types of research especially focused specifically on shrinking the process rules of the semiconductor patterns (2D lithography) [2]. However, few studies have explored its application to microstereolithography.

In the research field of semiconductor 2D lithography, a lateral process resolution improvement beyond the diffraction limit of freely propagating light has already been practically confirmed [16]. Therefore, in order to realize the proposed microstereolithography based on evanescent light exposure, an analysis of a fabrication capability specifically of the vertical resolution is urgently needed.

As the first step to realizing the proposed method, in this paper, we present a theoretical analysis of the characteristics of an evanescent light exposure. Furthermore, we show the results of an experimental verification of submicrometer thickness layer photopolymerization and an analysis of the process characteristics. Finally, we confirm the feasibility of using evanescent light in actual layer-lamination process on the basis of experimental results.

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Table 1
Characteristics of microstereolithography method.

	Two-photon polymerization	Layer -by-layer microstereolithography
Spatial process resolution	Submicrometer [Less than diffraction limit is possible because of multi-photon absorption]	About 1 μm (Lateral) [Due to diffraction limit of relatively longer working distance of projecting lens] About 5 μm (Vertical) [Due to surplus growth of propagating exposure light]
Process time	Low [Point scanning exposure]	High [Simultaneous surface exposure, especially in one-shot type]

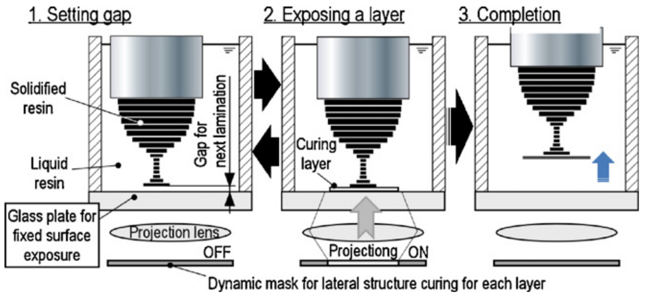

Fig. 1. One-shot layer-by-layer microstereolithography.

2. Microstereolithography using evanescent light

The concept of the proposed microstereolithography in a layer-based production fashion using evanescent light is shown in Fig. 2 in contract to the conventional propagating light exposure. Here, instead of a glass plate at the bottom for a fixed surface exposure, a solid immersion lens (SIL) is used as both a high-power imaging tool and a high-refractive-index material for total internal reflection (TIR). Under this condition, evanescent light exposure can be performed when light with an incident angle smaller than the critical angle is blocked from reaching the surface. A lateral resolution of the propagating light exposure is about 1 μm because the projection lens of a dynamic mask has a relatively long working distance due to the existence of a glass window, meaning a relatively larger numerical aperture (N.A.). In contrast, evanescent light exposure allows fine imaging with a lateral resolution on the order of 100 nm [17,18].

For vertical resolution characteristics in the case of the propagating light exposure, its minimum fabricatable layer thickness depends largely on the penetration depth of the light absorption of the photosensitive resin. Since the controllability of absorption property of photosensitive resin is limited, it is difficult to achieve a submicrometer thickness. Furthermore, the conventional propagating light can easily cause surplus growth of over 1 μm, especially around overhanging features, because some of the light travels through the cured resin layer, as shown on the left in Fig. 2. In contrast, with the proposed method, the penetration depth can be expected to strongly depend on the vertical localization of the evanescent light itself rather than the absorption characteristics of the photosensitive resin. This is why a submicrometer layer thickness resolution can be expected.

3. Theoretical analysis of evanescent light exposing layer

Prior to experimental analyses, theoretical analyses were carried out to determine the minimum possible resolution when considering both the penetration depth and vertical localization of evanescent light. Consider an evanescent light distribution $U(z)$ in the photosensitive resin along the depth z from the TIR interface as follows:

$$U(z) = \tau(\theta)U_0 \exp(-\alpha z)\exp\left(-\frac{4\pi n_2\sqrt{(n_1/n_2)^2\ \sin^2\ \theta - 1}}{\lambda_0}z\right), \quad (1)$$

where the first term $\tau(\theta)$, the second term U_0, the third exponential term, and the fourth exponential term physically represent a proportionality factor independent of the depth z [19], the energy of the incident light, the absorption efficient of the photosensitive resin based on the Lambert–Beer law, and the localizing factor for evanescent light based on Maxwell's equations, respectively. Further θ, α, λ_0, n_1, and n_2 denote the incident angle of the exposure light, the absorption efficient of the photosensitive resin, the wavelength of the incident light for exposure, and the refractive index of the SIL and photosensitive resin, respectively.

From Eq. (1), the curing layer thickness of the proposed method, C_d, can be described using the critical exposure energy of the resin U_c as follows:

$$C_d = \frac{\lambda_0}{\alpha\lambda_0 + 4\pi n_2\sqrt{(n_1/n_2)^2\ \sin^2\ \theta - 1}} \ln\frac{\tau(\theta)U_o}{U_c}. \quad (2)$$

Fig. 3 shows a plot of the curing layer thickness against the exposure energy of evanescent light from Eq. (2) under the following typical curing conditions: $\tau(\theta) = 2.52$ [19] (meaning p-polarization state), $n_1 = 1.78$, $n_2 = 1.51$, $\theta = 68^\circ$, $U_c = 100$ mJ/cm^2, $\lambda_0 = 488$ nm, and $\alpha = 100$ cm^{-1}. For comparison, the curing layer thickness with conventionally propagating light is also shown for the same conditions (but $\theta = 45^\circ$). From the figure, we see that the same incident light energy used in the conventional method can be employed for evanescent light photopolymerization. For example, at 3000 mJ/cm^2, the conventional method photopolymerizes a layer thickness over 100 μm, whereas evanescent light exposure photopolymerizes a thickness of under 1 μm.

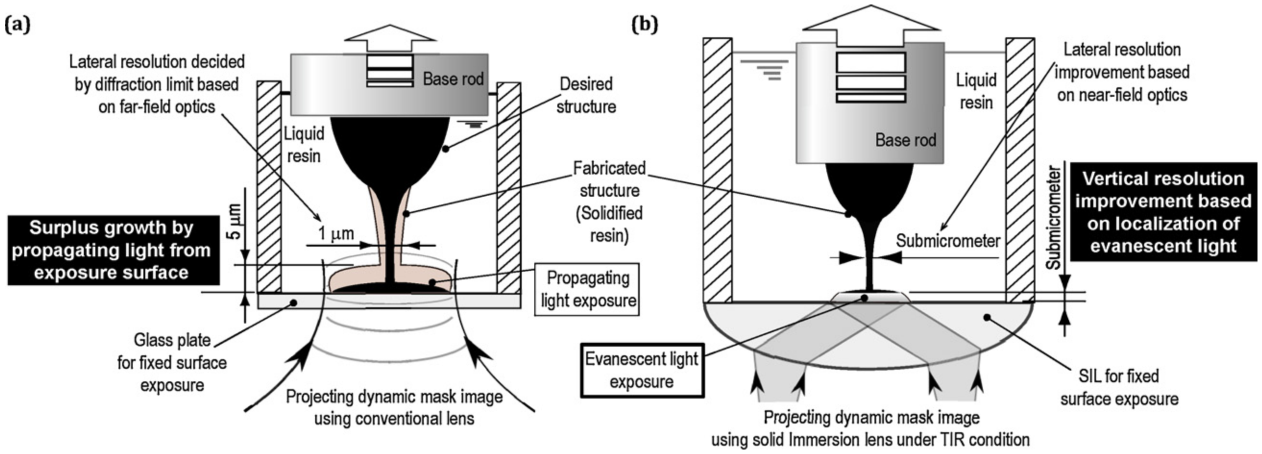

Fig. 2. One-shot layer-by-layer microstereolithography using propagating light (a) and using evanescent light (b).

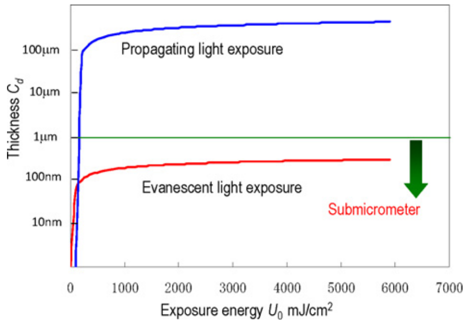

Fig. 3. Theoretically calculated cured layer thickness C_d against exposure energy U_0.

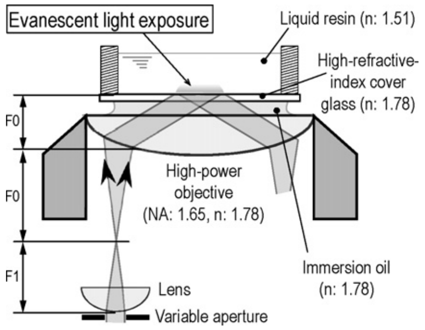

Fig. 4. Evanescent light exposure apparatus using objective.

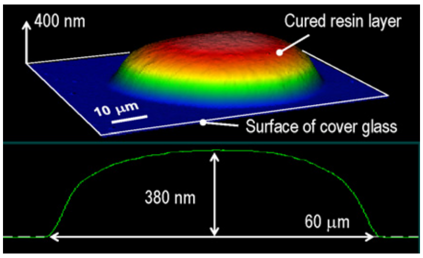

Fig. 5. Cured resin layer with evanescent light exposure.

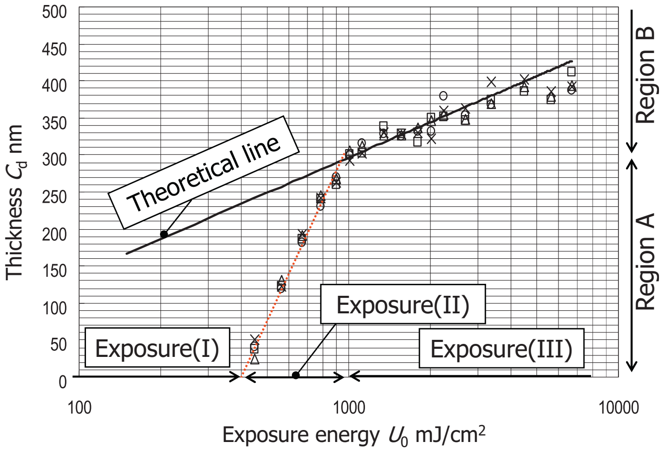

Fig. 6. Experimentally measured cured layer thickness C_d against exposure energy U_0.

4. Experimental analysis of evanescent light exposing layer

Fig. 4 shows the apparatus developed to study the cured layer thickness with evanescent light. A high-power objective (Olympus Corp., Apo100xOHR, NA: 1.65) was employed as a TIR medium to generate evanescent light. By offsetting an incident beam (λ_0: 488 nm) from the center-axis of the objective, as shown in the figure, the objective can act as a TIR medium. A free-radical type photosensitive resin (JSR Corp., KC1162, U_c: 44.4 mJ/cm^2, n: 1.51) was put on a special high-refractive-index cover glass (n: 1.78), which was located on the top surface of the objective (n: 1.78) with immersion oil (n: 1.78) as the refractive index matching material. The angle of incident light was set at 65°, which met the TIR conditions because the critical angle is 58°, and p-polarization state was selected. The variable aperture was set to 6 mm in diameter for a beam diameter of 60 μm on the expose surface. Fig. 5 shows the typical exposure results obtained with exposure energy of 2400 mJ/cm^2. A white light interferometer (Zygo Corp.: NewView 5000) showed that the evanescent light energy is sufficient for curing the photosensitive resin in the same manner as the conventional method and that a submicrometer layer thickness is possible.

Fig. 6 shows a plot of the thickness analysis against the exposure energy for the condition of 220 mW/cm^2 power. For comparison, the theoretical curve obtained using Eq. (2) is also shown. We see that the results for thicknesses greater than about 300 nm [exposure(III) range] almost meet the theoretical curve, although at lower thicknesses [exposure(II) range], the curing thickness characteristics are very different. This may be because of dissolved oxygen in the liquid resin. In general, during photopolymerization, free radicals induced by the incident light do not react immediately with the monomers of the resin but scavenge dissolved oxygen [exposure(I) range]. Indeed, photopolymerization only begins only once the monomers are able to compete with oxygen [20]. This seems especially important in the case of evanescent light, given the extremely steep light energy gradient in the strongly localized distribution. Dissolved oxygen would not be easily scavenged due to high diffusion rate of dissolved oxygen depending on the steep gradient, as schematically shown for region A (about 300 nm from the exposure surface) in Fig. 7. This may be the reason why the critical exposure energy (U_c: 44.4 mJ/cm^2) increased (386 mJ/cm^2). That is, photopolymerization only begins when the supply of dissolved oxygen from the near-field region (region B) around region A is overcome. Once photopolymerization occurs, that is, when the density of dissolved oxygen in region B has dropped, the cured thickness rapidly increases toward the theoretical level, where the evanescent light energy gradient is not so steep any more that diffusion of dissolved oxygen cannot prevent the photopolymerization as well as before. Though further analysis is required to understand the mechanism in greater detail, the standard deviation in cured layer thickness of 10 nm obtained at the region A suggests that the proposed method has sufficient controllability for submicrometer microstereolithography in a layer-based fashion.

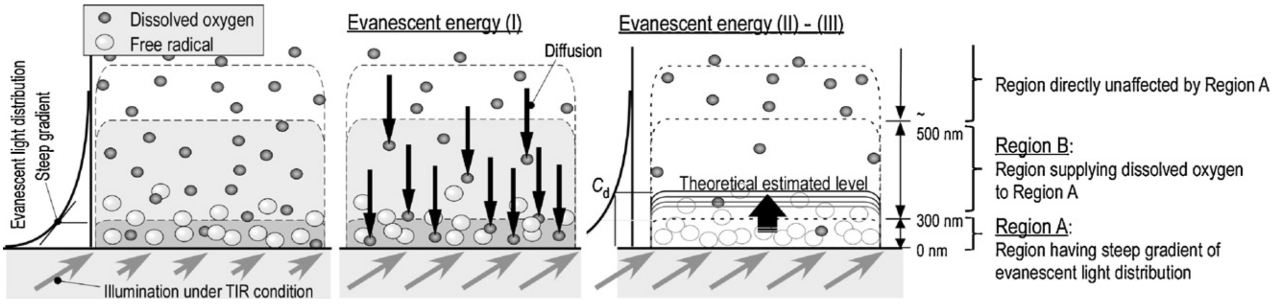

Fig. 7. Proposed photopolymerization mechanism for evanescent light exposure based on diffusion of dissolved oxygen.

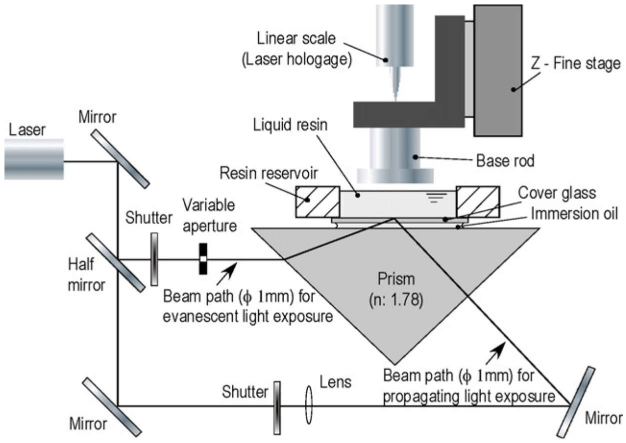

Fig. 8. Evanescent light exposure apparatus with cured layer lamination unit.

5. Compatibility with layer-by-layer microfabrication

We used the experimental apparatus shown in Fig. 8 to investigate whether the proposed method could be used to laminate a previously cured layer as a demonstration of layer-by-layer microfabrication. Here, a high refractive index prism (n: 1.78) was employed as the TIR medium. In addition, a mechanism to move the cured layer, mainly consisting of a base rod, fine Z-stage, and a linear scale with a resolution of 10 nm (Mitsutoyo Corp.: LGH-110), was installed from above, as shown in the figure.

In this experiment, as the first step, we focused on the confirmation of the essential feasibility of evanescent light exposure lamination in the following manner. First, propagating light exposure was performed for building up a cured resin substrate with a thickness of 10 μm. Next, evanescent light exposure was carried out with a layer gap of 300 nm (Fig. 9(a)). Fig. 9(b) indicates the optical microscopic image of the base rod surface, where we can clearly see the evanescent light curing thin layer on the propagating light curing base layer. An AFM observation verified that 300 nm thin layer can also be laminated on the pre-cured resin layer as well as by the conventional propagating light exposure method in a layer based production fashion (Fig. 9(c)).

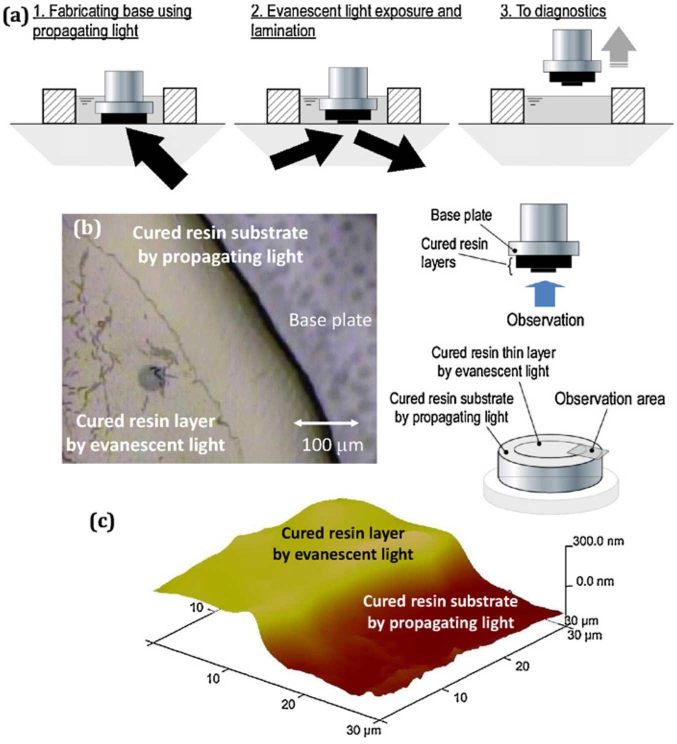

Fig. 9. Fundamental lamination experiment using evanescent light. (a) Lamination process, (b) optical microscope image, (c) atomic force microscopic image.

6. Conclusions

In this paper, we proposed the use of the spatially localized evanescent light instead of conventional freely propagating light in one-shot layer-by-layer stereolithography to achieve submicrometer spatial process resolution. The theoretical and experimental analyses, focusing on the vertical fabrication characteristics, can be summarized as follows: (1) A layer of submicrometer thickness can be fabricated using light energy levels equivalent to those used in the conventional method. (2) The photopolymerization mechanism with evanescent light has special characteristics: it has two modes that switch at a cure depth of about 300 nm. This may be because of the strong effect of dynamic diffusion of dissolved oxygen. (3) With an appropriate energy level, a standard deviation in layer thickness of less than 10 nm can be obtained. (4) The proposed method can also be applied to laminate a previously cured layer. These results suggest that the proposed method is a practical solution for achieving a submicrometer process resolution in three dimensions while maintaining the practical advantages of one-shot layer-by-layer exposure.

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