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Photofabrication of surface relief structure — mechanism and application

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Abstract

In order to elucidate the photoinduced surface relief (PSR) phenomenon on azobenzene polymer film, the formulation of the PSR formation process is established analytically from Navier–Stokes equation on the basis of our viscous fluid model. The experimental data obtained by the systematic studies for two-beam coupling and one-dimensional (1D) Gaussian beam irradiation are reproduced very well by the model calculation. The good coincidence assures the feasibility of our theoretical model. Furthermore, an example for applying this phenomenon to 2D micro-image recording and/or high-density optical data storage is presented.

Keywords: Photoinduced surface relief; Azobenzene polymer; Viscous fluid model; Micro-fabrication; High-density optical data storage

1. Introduction

Azobenzene functionalized polymers (azobenzene polymer) are very interesting and potentially useful materials for optical data storage, electro-optic modulation, optical switching and so on. In recent years, unique photoinduced surface relief (PSR) formation on azobenzene polymer films has been reported [1,2] and has attracted great attention [3–14]. Typical PSR examples observed by atomic force microscope are shown in Fig. 1. Large amplitude surface relief structures can be inscribed on thin films of azobenzene polymer upon the irradiation of appropriate light, which can induce the photoisomerization of the azobenzene moiety. Several experimental studies revealed that this phenomenon does not originate in the laser ablation process but in the macromolecular mass transfer from the bright region to the dark region. Thus, this phenomenon is quite different from other conventional micro-fabrication techniques such as photolithography, laser ablation and chemical etching. The PSR structure can be precisely controlled by the intensity, spatial distribution and polarization condition of the irradiated light and the irradiation time. Furthermore, though the PSRs are very stable unless the films are heated up to their glass transition temperature (T_g), the PSRs can be erased by heating the film above the T_g or the uniform light irradiation. Therefore, due to the facileness and the rewritable characteristic, this phenomenon is expected to be applicable for active optical device fabrication, ultra-high-density optical data storage and so on.

Besides the research field of applied optics, the mechanism of the PSR formation has also attracted great attention from the standpoint of fundamental polymer physics. Since this phenomenon is a result of unusual large-scale photo-driven mass transport process. Surprisingly, it is carried out on the solid state thin film at a temperature much below the T_g of the polymer. Although several models have been recently proposed to account for the mechanism of PSR formation [15–18], the problem is still controversial and no feasible model with sufficient physical background has ever been proposed. Therefore, in order to discuss the dynamics of PSR formation more precisely and comprehensively, we have examined a systematic study in the framework of our viscous fluid model [18]. In this paper, the validity of our viscous fluid model will be elucidated and some application for microscopic image recording will be referred.

2. Analytical background

2.1. Interference fringe pattern irradiation

Here, an interference light pattern produced by two-beam coupling of coherent laser beam is considered as an

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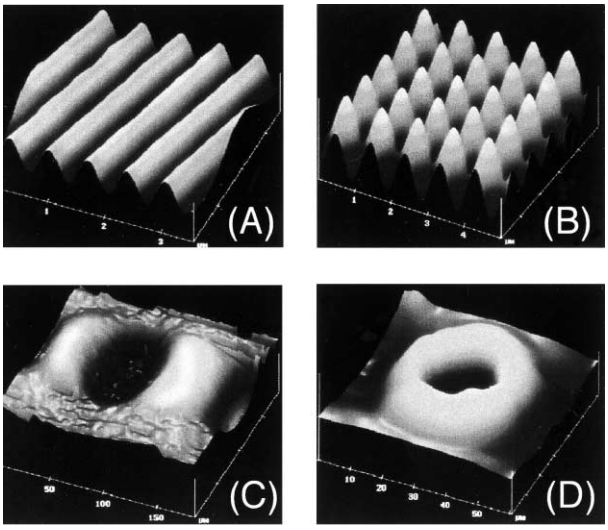

Fig. 1. Typical AFM images of the surface relief structure on films of azobenzene polymer: (A) 1 μm pitch grating; (B) orthogonal gratings are fabricated by 1 μm pitch interference light pattern; (C) and (D) are approximately 30 μm diameter pits fabricated by focused linearly and circularly polarized laser beams, respectively.

excitation light for the PSR fabrication. Light intensity in azopolymer film $I_{\sin}$ brought by two-beam interference is expressed by the following equation since it decays exponentially in the y-direction attributed to the light absorption of the azobenzene

$$I_{\sin}(x, y) = I_0 \, \mathrm{e}^{\alpha(y-h)} \cdot \tfrac{1}{2} (\cos kx + 1) \tag{1}$$

where I_0, α and k denote the maximum intensity, the absorption coefficient and the interference wavenumber corresponding to the pitch of interference fringe, respectively. A schematic illustration of the proposed viscous fluid model is shown in Fig. 2. The y-coordinate is so defined that $y = 0$ at the interface between polymer and glass substrate and $y = h$ at the surface of the polymer. The film is irradiated with laser light from its surface side. This experimental geometry provides the boundary conditions of the fixed end at the interface between polymer and substrate, and that of the free end at the surface of the film. Taking many experimental results hitherto reported into account [9,15,18], the driving force is assumed to be proportional to the first order

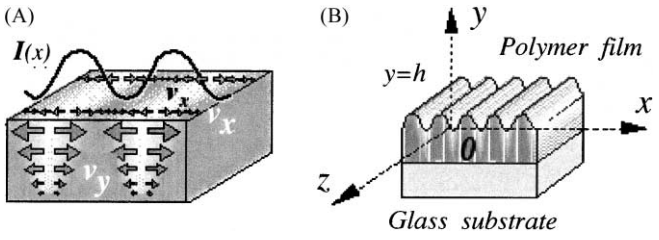

Fig. 2. (A) Schematic illustration of the proposed model and (B) the definition of the coordinate system.

differentiation of the light intensity profile ($I(x, y)$) with respect to x-direction. Then the distribution of the driving force along the x-direction is described as follows:

$$F_{\sin}(x, y) = I_0 \frac{\partial}{\partial x} \mathrm{e}^{\alpha(y-h)} \cdot \frac{1}{2}(\cos kx + 1)$$

$$= -\frac{1}{2} I_0 k \, \mathrm{e}^{\alpha(y-h)} \sin kx \tag{2}$$

We assume that azopolymer behaves as a viscous fluid in the PSR forming process and the mass transfer occurs as a result of bulk deformation brought by the driving force. Then, the simplified Navier–Stokes equation describing the dynamics of the system can be expressed as follows:

$$0 = \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{1}{\mu} F_x(x, y) \tag{3}$$

where v_x, μ and $F_x(x, y)$ are the x-component of the velocity of mass transport, the viscosity and the body force acting on the polymer as a viscous fluid, respectively.

Applying the condition of incompressibility ($\partial v_x/\partial x + \partial v_y/\partial y = 0$) and appropriate boundary conditions ($v_x|_{y=0} = 0$, $v_y|_{y=0} = 0$), the rate of PSR formation for sinusoidal distribution of light intensity $R_{\sin}$ is obtained finally in the following equation:

$$R_{\sin}(x) = \frac{\partial h}{\partial t} = v_y|_{y=h} = \frac{-I_0 k^2 \cos kx}{2\mu(k^2 - \alpha^2)}$$

$$\times \left[\frac{1}{\alpha} - \frac{\alpha}{k^2} - \frac{1}{\alpha} \mathrm{e}^{-\alpha h} + \frac{2\alpha + k \, \mathrm{e}^{-\alpha h}(\mathrm{e}^{-kh} - \mathrm{e}^{kh})}{k^2(\mathrm{e}^{-kh} + \mathrm{e}^{kh})} \right] \tag{4}$$

Additionally, polynomial behavior of the function $R_{\sin}$ (at $x = 0$) in the limit of $h \to 0$ and $h \to \infty$ are expressed as

$$\lim_{h \to 0} R_{\sin}(k, \alpha, h) = \frac{I_0 k^3 h^3}{6\mu} \propto h^3 \tag{5}$$

$$\lim_{h \to \infty} R_{\sin}(k, \alpha, h) = \frac{I_0}{6\mu\alpha} = \text{const.} \tag{6}$$

2.2. 1D Gaussian beam irradiation

In addition, though the formulation above is for the sinusoidal light pattern irradiation, it is able to extend to the non-periodic Gaussian beam irradiation on the basis of Fourier transformation. A profile function of 1D Gaussian distribution is expressed with Gaussian width σ and is derived as following using an inverse Fourier transformation

$$I(x, y) = I_0 \, \mathrm{e}^{\alpha(y-h)} \, \mathrm{e}^{-(x^2/2\sigma^2)}$$

$$= \sqrt{\frac{2}{\pi}} I_0 \, \mathrm{e}^{\alpha(y-h)} \int_0^\infty \sigma \, \mathrm{e}^{-(k^2\sigma^2/2)} \cos kx \, \mathrm{d}k \tag{7}$$

Thus the force distribution F_{Gauss} brought by the intensity distribution above can be described as follows:

$$F_{\text{Gauss}}(x, y) = I_0 \frac{\partial}{\partial x} e^{\alpha(y-h)} e^{-(x^2/2\sigma^2)}$$
$$= -\sqrt{\frac{2}{\pi}} I_0 e^{\alpha(y-h)} \int_0^\infty k\sigma e^{-(k^2\sigma^2/2)} \sin kx \, dk$$
$$= 2\sqrt{\frac{2}{\pi}} \int_0^\infty \sigma e^{-(k^2\sigma^2/2)} F_{\sin}(x, y) \, dk \quad (8)$$

Based on the linearity of the theory, the similar relationship as found in F_x between general function and its Fourier components should also be established in the rate of PSR formation R. Therefore, R corresponding to the 1D Gaussian beam R_{Gauss} is described by the following equation:

$$R_{\text{Gauss}}(x) = 2\sqrt{\frac{2}{\pi}} \int_0^\infty \sigma e^{-(k^2\sigma^2/2)} R_{\sin}(x) \, dk \quad (9)$$

3. Experimental

An azobenzene polymer (PMD36) was obtained by radical copolymerization of 4-(*N*-(2-methacryloyloxyethyl)-*N*-ethylamino)-4′-nitroazobenzene and methyl methacrylate, whose degree of azo functionalization is 36 mol%. Details of this synthesis have been reported in the literature [14]. Amorphous thin films of PMD36 with good optical quality were prepared on glass substrates by spin coating from dichloromethane solution. The absorption coefficient of the PMD36 film at 488 nm was 12.3 μm^{-1}. The thickness of the films was measured by a mechanical stylus profiler (Alpha-Step 300, KLA-Tenkor). The surface relief structure of the film was observed by atomic force microscope (Nanoscope IIIa, Digital Instruments) in a tapping mode under ambient condition.

Optical setups for each experiment are depicted in Fig. 3. The 488 nm line from an Ar^+ laser was employed for light irradiation. Fig. 3(A) is for the two-beam coupling to generate the interference fringe pattern for grating formation. Light irradiance before beam coupling was fixed to about 30 mW/cm^2. Fig. 3(B) is for the 1D Gaussian beam irradiation produced by focusing a collimated Gaussian beam with a cylindrical plano-convex lens. In practice, the Gaussian width of the focused beam σ was controlled by the diameter of collimated incident laser beam, which can be changed by focal length of the collimating lens and its position. Light irradiance at the beam center ($x = 0$) and irradiation time were set to about 160 mW/cm^2 and 60 min, respectively, in order not to affect unexpected photo-bleaching effect or laser ablation. Fig. 3(C) shows a simple setup for the 2D micro-image recording. The pattern regenerated by a computer-generated hologram (CGH) is reduced and focused on the polymer surface by the objective lens. Laser beams with different polarization plane were achieved by rotating a half-wave plate to give a linear polarized light.

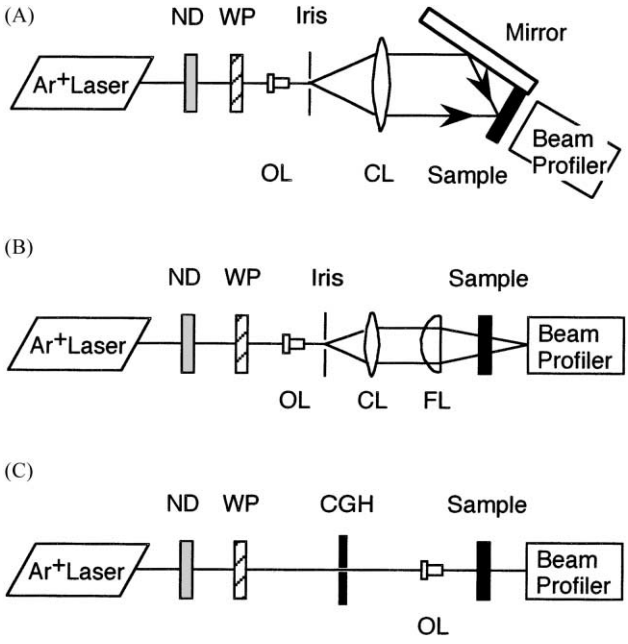

Fig. 3. Optical arrangements for each experiment: (A) and (B) are for the two-beam coupling and the 1D Gaussian beam irradiation experiment, respectively; (C) is for the 2D micro-image recording. ND is a variable neutral density filter. WP is a quarter-wave (or a half-wave) plate. OL, CL and FL are an objective, a collimating and a focusing cylindrical lens, respectively.

By replacing the half-wave plate with a quarter-wave plate or a pseudo-depolarizer, circularly polarized and unpolarized beams were also supplied, respectively. The profile of the incident beam was monitored by a laser beam profiler (LEPAS-11, Hamamatsu Photonics K.K.).

4. Results and discussions

A systematic study of the PSR photofabrication process has been performed regarding the influence of experimental and geometrical parameters. Fig. 4 shows the experimental results for two-beam coupling experiment: (A) the inscrip-

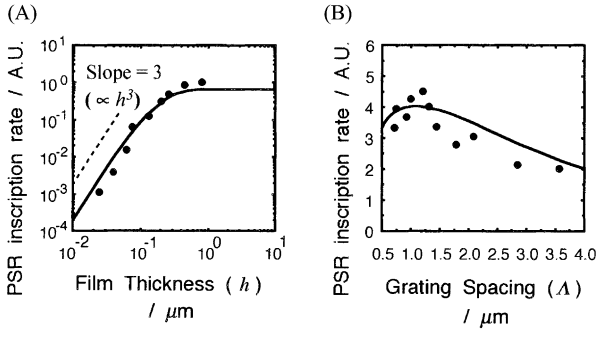

Fig. 4. The dependence of the SRG inscription on: (A) the film thickness h; (B) the interference pattern spacing Λ. (A) is in a log–log plot, while (B) is in a linear plot. The solid line is the theoretical curve.

tion rate dependence on the film thickness h and (B) dependence on the grating spacing Λ that is related to the grating wavenumber k as $k = 2\pi/\Lambda$. The experiment was carried out under circularly polarized light irradiation on condition of photon dose 14 and 7 J/cm^2, film thickness 1.0 and 0.8 μm and absorption coefficient 12.3 μm^{-1}, respectively. The solid lines in the figure show the theoretical curves calculated by Eq. (4) with the specific experimental parameters. For the thickness dependence, as was predicted by Eqs. (5) and (6), cubic dependence ($\propto h^3$) of the PSR grating inscription rate in the thin region and an asymptotic tendency in the thick limit of the film were observed. In the same manner, the dependence of the PSR grating inscription rate on the grating spacing is shown in Fig. 4(B). In this case, since the x-component of the irradiating electric-field changing accompanied with the variation of two-beam coupling angle θ (θ is related to Λ as $\Lambda = \lambda/2\sin\theta$), the factor of $\cos^2\theta/\Lambda$ should be added in the term of driving force (I_0 in Eq. (4)) as a geometrical calibration factor. With this calibration factor, the theoretical curve is almost in a good agreement with the experimental data as shown in the figure. Since no fitting parameter is excepted for the factor, I_0/μ was used in the model calculation, it is reasonable to conclude that this quantitative agreement throughout the whole experimental range suggests the feasibility of our viscous fluid model.

The validity of our model could also be confirmed in the 1D Gaussian beam irradiation. As shown in Fig. 5(A), the PSR of Mexican-hat profile obtained by the laser beam with 1D Gaussian distribution. The cross-section profile and the corresponding theoretical curve calculated by Eq. (9) with the value of $\sigma = 2.3$ μm are shown in Fig. 5(B). The experiment was carried out on a condition of photon dose 1.1×10^3 J/cm^2 (at $x = 0$), film thickness 0.7 μm and absorption coefficient 12.3 μm^{-1}, respectively. The theoretical curve agrees well with the experimental data. (The shallow depressions observed around $x = \pm 8$ μm are attributed to an imperfection of irradiated 1D Gaussian beam that has weak satellite peaks due to the Fresnel diffraction.) In our experimental conditions, the aspect ratio of the irradiated beam pattern was large enough though it was varied from 100 to 2000 depending on each experimental condition, and then

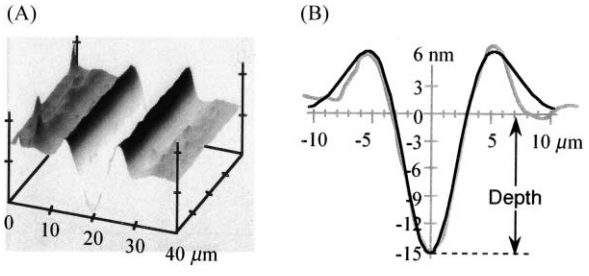

Fig. 5. (A) Topographic image of the PSR inscribed by 1D Gaussian beam with linear polarization along the direction of light intensity gradient. (B) Cross-section profile of the surface deformation obtained by AFM (thick gray line) and a numerical simulation calculated by Eq. (9) (thin black line).

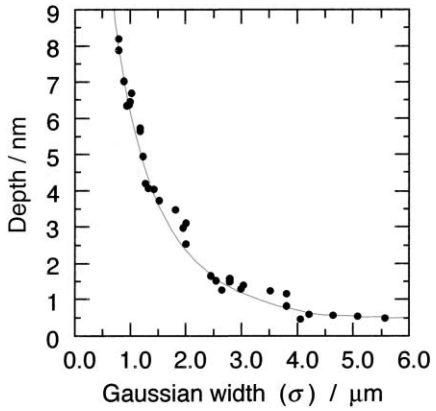

Fig. 6. Gaussian width σ dependence of the PSR depth inscribed by the irradiation of 1D Gaussian beam. Solid line indicates the theoretical curve calculated by Eq. (9).

the gradient of the light intensity along the longitudinal direction was negligible in comparison with that of the lateral direction. Therefore, PSR formation along the longitudinal direction of the 1D Gaussian beam was not appreciable.

Fig. 6 shows a result how the inscription depth of the PSR is influenced by the Gaussian width σ. The experiment was carried out on condition of photon dose 5.8×10^2 J/cm^2 (at $x = 0$), film thickness 1.1 μm and absorption coefficient 12.3 μm^{-1}, respectively. It is clear from the figure that the inscription depth at a certain irradiation time (i.e., the inscription rate) monotonously decreases with increasing Gaussian width of the beam and the theoretical curve calculated by Eq. (9) with the fitting parameter $I_0/\mu = 240$ agrees quite well. This good coincidence assures again that our viscous fluid model is feasible to describe the dynamics of the PSR formation.

Another point of view, a significant conclusion can be extracted from the result of the Gaussian width dependence. Namely, achieving the irradiated light pattern more minute, the inscription rate of the PSR increases and then the structure can be inscribed faster. This characteristic of this phenomenon is very favorable for micro-fabrication and/or high-density optical data recording.

We have tried to make use of this favorable characteristic for 2D minute relief image recording as the first attempt. Fig. 7 shows the topographic image observed by atomic force microscope of the photofabricated Chinese character array that is generated by a CGH and a phase mask. Dark and bright area in the characters corresponds to subsidence and upheaval, respectively. Circularly polarized light beam from Ar^+ laser (488 nm) was irradiated with the intensity of 200 μW for just 1 min. The irradiance of the writing beam is approximately 300 mW/cm^2. Dimensions of each Chinese character are 15×15 μm^2. Though the minimum line width achieved in this experiment was approximately 2 μm, it could be possible to make it more thinner if we can take into consideration of the complex amplitude distribution of images on designing and manufacturing a CGH.

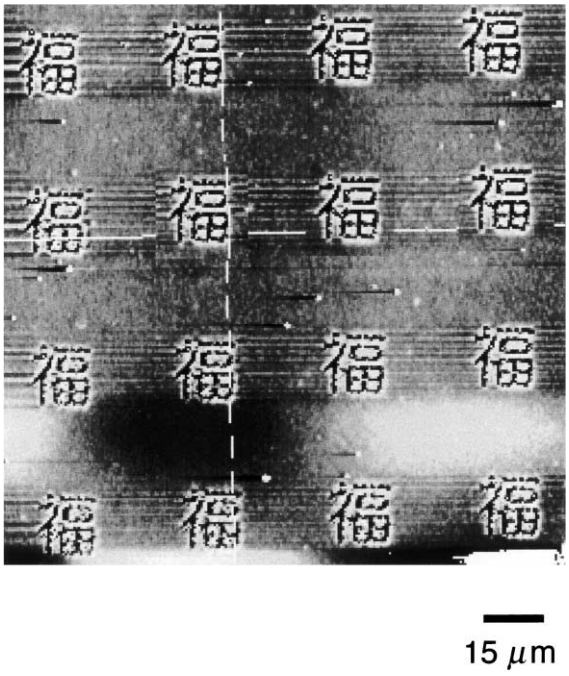

Fig. 7. Topographic PSR image of a Chinese character array fabricated on azobenzene polymer film observed by AFM. The depth of the PSR is approximately 20 nm.

That technique is called as "super-resolution technique" and that allow us to generate any light patterns not only in micro-meter scale but also in nano-meter scale resolution (up to $\lambda/4\,\mathrm{NA}$; NA = numerical aperture).

5. Conclusion

In this study, we established a theoretical model for PSR formation and the experimental data obtained by the systematic study could be explained sufficiently. Our formulation is not only a useful tool for the analysis of the PSR fabrication process but also is a good guide to design and/or synthesize new materials for the opto-electronic device application.

We have succeeded to fabricated micro-images by irradiating 2D beam patterns using CGH, based on the PSR formation on azobenzene polymer films. Since this is facile one-step and purely optical process without any subsequent processes such as developing, fixing and cleaning, therefore this is one of the promising new technology for micro-fabrication and/or high-density optical data storage.

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