

## Analysis of Surface Relief Gratings on Azo Polymer Films

Cha-Hwan OH,\* Ui-Jung HWANG and Jung-Sung KIM

*Department of Physics & Quantum Photonic Science Research Center, Hanyang University, Seoul 133-791*

Yong-Sung KIM, Jae-Hwang LEE, Chang-Hwan KIM and Kai-Ming HO

*Ames Laboratory-U. S. Department of Energy and Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, U.S.A.*

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Photoinduced surface relief gratings (SRGs) formed on Azo polymer films by using a two-beam interference technique were observed and analyzed. The heights of the SRGs at various polarization combinations of two writing beams were measured and compared with the force distributions from various theoretical models. As a result, we could suggest a combined model of the optical gradient force model and the pressure gradient force model by which the measured data could be explained well.

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### I. INTRODUCTION

Azo polymers have received great attention in the field of optical information processing, such as holographic optical data storage, diffractive optical elements, LC anchoring, photonic crystal fabrication, and so on [1–6], because of their high nonlinearity, stability, and reversibility. When azo polymers are illuminated by polarized light, two effects can arise. One is the molecular re-orientation effect, and the other one is the molecular migration effect [7–14]. As for molecular re-orientation, the mechanism is well known to be the results of a photoisomerization process [9,11]. A rod-like trans isomer of an azo molecule is oriented perpendicular to the polarization direction of the light by repeating the photoisomerization process owing to the selective angular absorption of the trans conformers, which brings a birefringence to the polymeric film.

As for the molecular migration, several models have been suggested to explain the surface relief grating (SRG) formed on an azo polymer film by using the two-beam interference technique [13–18]. Kumar *et al.* suggested an optical gradient force model [13, 14]. They showed that the SRG formation strongly depended on the polarization directions of the writing beams and excellently explained experimental results with their model. For examples, SRG formation in the case of an orthogonal polarization combination, such as (45°, 135°) or (RCP, LCP), as well as in the case of a parallel polarization combination, such as (p, p), can be expected from

their model. However, although this model explains the polarization dependence of SRG formation fantastically, it's still not perfect for explaining the SRGs quantitatively at all other polarization combinations. For example, most papers have reported that the heights of the SRG in the case of (45°, 135°) or (RCP, LCP) are higher than that in the case of (p, p), which is contradicted by the model. Also, it is widely known that a SRG can be formed in the case of (s, s) or (p, s) even though the heights are too small, but the optical gradient force model gives no SRG for the (s, s) or the (p, s) polarization combination. Therefore, an additional effect or at least a correction needs to be considered in the optical gradient force model.

As a good candidate for the correction to the optical gradient force model, we consider pressure gradient force model suggested by Barrett *et al.* [15,16]. In that model, the increase in volume required during the photoisomerization of the azobenzene leads to an increase in pressure within the film, and the spatial pressure gradient induced by interfered intensity modulation on the film is sufficiently high to induce the polymer flow to generate the SRG. Since this pressure is induced by a photoisomerization process that depends on the light intensity, the pressure gradient is equivalent to the intensity gradient. Thus, this model can explain the SRGs formed by parallel polarization combinations of writing beams. This model, however, cannot explain well the dramatic effects of the polarization states of the writing beams. Moreover, the higher SRG height in the case of orthogonal polarization combinations, such as (45°, 135°) and (RCP, LCP), cannot be understood from this

\*E-mail: choh@hanyang.ac.kr

model. Nevertheless, only this model can explain the SRG in the case of the polarization combination of (s, s).

In this research, we prepared a novel experimental procedure to measure successively the SRG height for a complete set of linear polarization combinations. If the height of SRGs are to be predicted precisely, a rigorous calculation for the fluid dynamical equation taking into account the driving force, the surface tension, and the viscosity of the polymer film should be carried out. However, if the intensity of light is low enough not to cause any nonlinear effect or chemical deformation, we can assume the height to be proportional to the driving force. And, in this study, we compared the measured height of SRG with the force distributions by using the optical gradient force model and the pressure gradient force model in order to examine the two models.

## II. EXPERIMENTS

### 1. Polymer Sample

A malonic ester monomer (MCR1) was synthesized by reacting in tetrahydrofuran (THF) at 0 °C for 24 hour malonyl dichloride and disperse red 1. It was then condensed with 1,6-dibromohexane in THF in the presence of sodium hydride at 65 °C for 24 h to give poly(malonic ester) (PDR1) with two symmetrical disperse red 1, a photoresponsive group. A more detailed preparation procedure is in the Ref. 19. The polymer thin films were cast from the polymer solution (5 wt%) in  $\text{CHCl}_3$  onto a glass plate for 30 seconds by using a spin coater.

### 2. Experimental Setup

Surface relief gratings are inscribed on the Azo polymer film by using a conventional two-beam interference technique. As Figure 1 shows, a Nd:YAG laser at 532 nm was used for writing the grating. The two beams formed

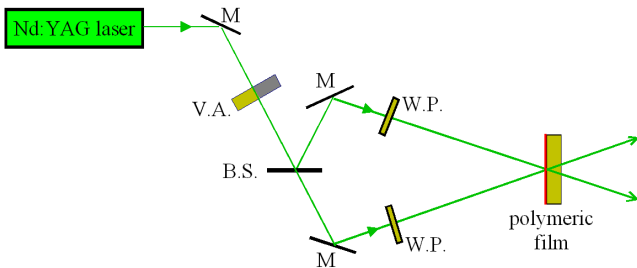


Fig. 1. Experimental setup for inscribing the grating by using the two beam interference technique. (M : mirror, V.A. : variable attenuator, B.S. : beam splitter, W.P. : wave plate.)

by a beam splitter illuminated the polymer film. The polarizations of the writing beams could be adjusted by using half-wave plates. The polymer film was spin coated on the slide-glass substrate, and the thickness of film was measured by using an  $\alpha$ -step profiler. The topography of the inscribed SRG was obtained by using atomic force microscopy (XEI-100, PSIA) to determine the height of the relief grating.

### 3. Theoretical Calculation

The coordinates used in this calculation for the two-beam interference arrangement is depicted in Figure 2. Two coherent beams, 1 and 2, of arbitrary linearly polarized waves interfere symmetrically on the sample. The two beams intersect at an angle  $\theta$  on the sample plane.

The two incident writing beams interfere and can be represented by

$$E_1 = E_0 \begin{pmatrix} \cos 2\psi_1 \cos \theta \\ \sin 2\psi_1 \\ -\cos 2\psi_1 \sin \theta \end{pmatrix} e^{i(k_1 \cdot r - \omega t - \frac{\pi}{2} - \varphi)},$$

$$E_2 = E_0 \begin{pmatrix} \cos 2\psi_2 \cos \theta \\ \sin 2\psi_2 \\ \cos 2\psi_2 \sin \theta \end{pmatrix} e^{i(k_2 \cdot r - \omega t - \frac{\pi}{2} - \varphi)}, \quad (1)$$

where  $E_0$  means the electric field amplitude,  $\psi_1$  and  $\psi_2$  the angles between p-polarization directions and the optic axes of half-wave plates,  $\varphi$  the absolute phase retardation caused by the wave plate, and  $k_1$  and  $k_2$  the propagation wave vectors of the beams, respectively:

$$k_1 = k_0 \begin{pmatrix} \sin \theta \\ 0 \\ \cos \theta \end{pmatrix}, \quad k_2 = k_0 \begin{pmatrix} -\sin \theta \\ 0 \\ \cos \theta \end{pmatrix} \quad (2)$$

In Eq. (1), arbitrary linear polarized waves can be obtained by changing the angles of the half-wave plates,

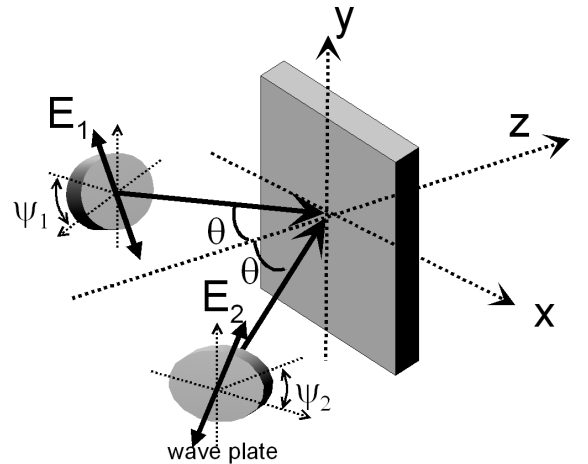


Fig. 2. Schematic representation of two interfering arbitrarily polarized waves on the film.

$\psi_1$  and  $\psi_2$ , from 0 degrees at which the polarization state is p polarization.

The total electric field of the superposed waves is given by

$$E = E_0 \begin{pmatrix} \cos \theta (\cos 2\psi_1 e^{i\delta} + \cos 2\psi_2 e^{-i\delta}) \\ \sin 2\psi_1 e^{i\delta} + \sin 2\psi_2 e^{-i\delta} \\ -\sin \theta (\cos 2\psi_1 e^{i\delta} - \cos 2\psi_2 e^{-i\delta}) \end{pmatrix} \times e^{i(\eta - \varphi - \frac{\pi}{2} - \omega t)}, \quad (3)$$

where  $\delta = k_0 x \sin \theta$  and  $\eta = k_0 z \cos \theta$ . The material will see the electric field distribution given by Eq. (3). In this expression, the phase shift due to the refractive index of the material and the intensity change due to the absorption of the material were ignored.

The optical gradient force induced by the electric field of the writing beams suggested by Kumar *et al.* [15,16] is given by

$$\mathbf{F} = \frac{1}{2} \varepsilon_0 \chi (\mathbf{E}(\mathbf{r}) \cdot \nabla) \mathbf{E}(\mathbf{r}), \quad (4)$$

where  $\varepsilon_0$  and  $\chi$  denote the electric permittivity of vacuum and the real part of the electric susceptibility of the polymer, respectively. Now, the force expressed by Eq. (4) can be rewritten as multiples of the electric-field components and their derivatives. Mass migration occurs along the direction of the grating vector, *i.e.*, the direction of the force of the grating vector, which is the  $x$ -axis in Figure 2. Thus, the deriving force is expressed by

$$\mathbf{F}_x = \frac{1}{2} \varepsilon_0 \chi \left( E_x \frac{\partial E_x}{\partial x} + E_y \frac{\partial E_x}{\partial y} + E_z \frac{\partial E_x}{\partial z} \right). \quad (5)$$

For arbitrary linearly polarized writing beams,  $(2\psi_1, 2\psi_2)$ , the force is calculated as

$$\mathbf{F}_x = -\varepsilon_0 \chi \mathbf{E}_0^2 k_0 \cos^2 \theta \sin \theta \cos 2\psi_1 \cos 2\psi_2 \sin 2\delta. \quad (6)$$

As for the pressure gradient force, it is proportional to the intensity distribution given by

$$I = 2\mathbf{E}_0^2 (1 + \cos 2\delta (\cos 2\psi_1 \cos 2\psi_2 \cos 2\theta) + \sin 2\psi_1 \sin 2\psi_2). \quad (7)$$

Figure 3 shows the calculated results for the specific polarization combination of writing beams (p, p). The bold lines represent the polarization directions and the magnitudes of field. The optical gradient force (solid line) and the intensity distribution (dotted line) were calculated by using Eq. (6), and (7), respectively.

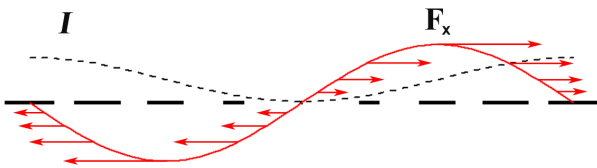


Fig. 3. Calculated optical gradient force (solid line) and intensity distribution (dotted line) along the  $x$ -axis for the  $(0^\circ, 0^\circ)$  polarization combination of the writing beams.

### III. RESULTS AND DISCUSSION

#### 1. Surface Relief Profiles

The SRGs for various polarization combinations of writing beams were investigated. The thickness of the film spin coated on the slide glass was measured to be 170 nm. The intensities of the writing beams and the writing time were fixed to 178 mW/cm<sup>2</sup> and 5 min, respectively.

Figure 4 shows examples of measured topographical images of SRGs at two polarization combinations of writing beams. As the figure shows, the height of the SRG sensitively depends on the polarization states of the writing beams although the intensities of the writing beams and the writing time were the same. Through separate experiments for SRGs at various polarization combinations of the writing beams, we confirmed that the polarization combination (RCP, LCP) had the largest SRG height while a very small SRG height was formed for the polarization combination (s, s). The polarization combinations that made efficient SRG heights were, in order, (RCP, LCP),  $(45^\circ, 135^\circ)$ , (p, p), (RCP, RCP), (p, s), and (s, s). This order for the relative height is quite general and refers to many experimental results [20].

#### 2. Height of SRGs with the Polarization States of Writing Beams

We examined the polarization dependence of the height of the SRG by preparing a novel experimental procedure as follows: Firstly, in the  $45^\circ$ -fixed experiment, the polarization state of one writing beam was fixed to  $45^\circ$ , and the polarization state of the other was varied from  $0^\circ$  to  $180^\circ$ . The first polarization combination  $(45^\circ, 0^\circ)$  and the last one  $(45^\circ, 180^\circ)$  are identical configurations. The direction of the angle of polarization was varied by  $5^\circ$  to  $20^\circ$  during the experiment.

In the next experiment, pp-ps-ss, the polarization direction of one writing beam was fixed to a p polarization, that is,  $0^\circ$ , and that of the other writing beam was varied from p to s polarization, that is,  $0^\circ$  to  $90^\circ$ . Again, the polarization direction of one writing beam was fixed to s polarization, that is,  $90^\circ$ , and that of the other writing beam was varied from p to s polarization, that is,

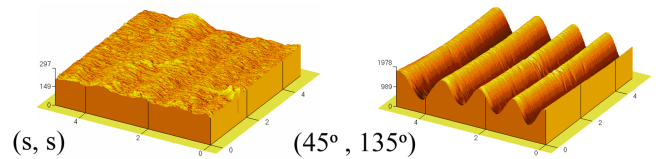


Fig. 4. Topographic images of surface relief gratings inscribed by different polarization combinations of the writing beams.

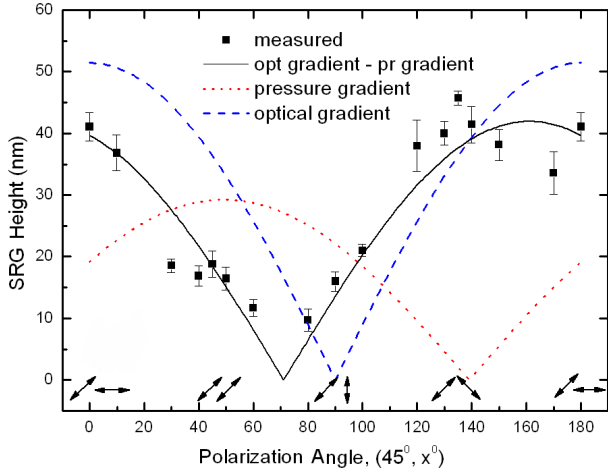


Fig. 5. Measured SRG height and calculated optical gradient force (dashed line) and intensity modulation amplitude (dotted line) in  $45^\circ$ -fixed experiment.

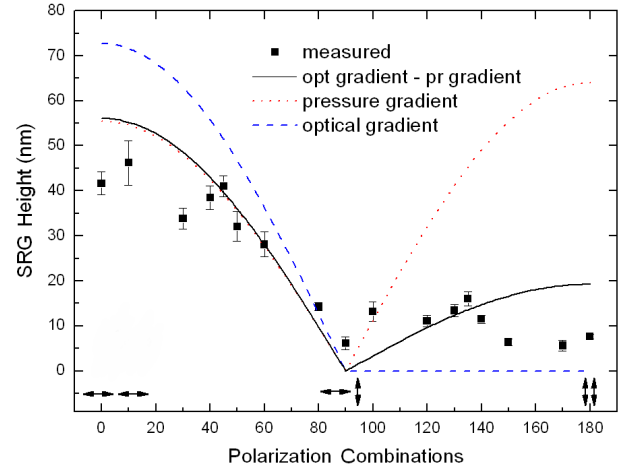


Fig. 6. Measured SRG height and calculated optical gradient force (dashed line) and intensity modulation amplitude (dotted line) in the pp-ps experiment.

$0^\circ$  to  $90^\circ$ . The experiments pp-ps and ps-ss are shown together in a graph for convenience. The SRGs were inscribed at at least three different points on the same film for each polarization combination and were examined by AFM at least three times for the SRG of one point.

Figure 5 and 6 show the measured heights of the SRGs for various polarization combinations of the writing beams. Figure 5 shows the measured heights of the SRGs in the  $45^\circ$ -fixed experiment. When the polarization combination was  $(45^\circ, 0^\circ)$ , the height of the formed SRG was measured to about 40 nm. The height of the SRG, however, decreased as the polarization direction of the writing beam increased from  $0^\circ$ . The smallest SRG was formed near  $(45^\circ, 70^\circ)$ . The height increased again as the polarization direction of the writing beam increased above  $70^\circ$ , and the largest SRG was formed near  $(45^\circ, 135^\circ)$ . The height decreased after that until the direction of the polarization came to  $(45^\circ, 180^\circ)$ , which was identical to the initial polarization combination,  $(45^\circ, 0^\circ)$ . Figure 6 shows the measured heights of the SRG in the pp-ps-ss experiment. The height of the SRG at the polarization combination of the writing beams of  $(0^\circ, 0^\circ)$  decreased as the polarization combination was changed toward  $(0^\circ, 90^\circ)$ . The height of the SRG increased as the polarization combination was changed toward  $(90^\circ, 90^\circ)$ , but after  $(135^\circ, 90^\circ)$  to  $(90^\circ, 90^\circ)$ , decreased, rather than increase, gradually.

In Figures 5 and 6, the dashed and the dotted lines represent the relative optical gradient force and the pressure gradient force (intensity modulation amplitude) with the polarization states of the writing beams, respectively. As the figures show, each force variation does not match a measured height variation of a SRG with a polarization state. For example, in Figure 5, the optical gradient force anticipates no SRG on  $(45^\circ, 90^\circ)$  and a large SRG on  $(45^\circ, 0^\circ)$  or  $(45^\circ, 180^\circ)$ , but a moderate SRG was inscribed on  $(45^\circ, 90^\circ)$ . The pressure gradient force pro-

portional to the intensity modulation amplitude anticipates a large SRG on  $(45^\circ, 45^\circ)$ , which is a parallel polarization combination, and no SRG on  $(45^\circ, 135^\circ)$ , which is an orthogonal polarization combination. The experimental results, however, showed moderate SRG near  $(45^\circ, 45^\circ)$  and a large SRG near  $(45^\circ, 135^\circ)$ . Also, as Figure 6 shows, although the optical gradient force model anticipates no SRG from  $(90^\circ, 0^\circ)$  to  $(90^\circ, 90^\circ)$ , experimental measurement confirm that a SRG was certainly formed in this region of writing beam polarizations.

If we notice that the pressure gradient force changes (dotted line) with the polarization angle, it is reasonable to consider the pressure gradient force, as well as the optical gradient force, in order to explain the experimental results more nicely. Also, the measured data in Figure 5 and Figure 6 were fitted to sum of Eq. (6) and Eq. (7) by adjusting the weight factor for each equation. The solid lines in Figure 5 and Figure 6 show the fitting results. As one can see in the figures, the solid lines show better agreement with the measured heights than the dashed or the dotted line. In these calculations, the weight factors of the optical gradient force and the pressure gradient force were about 0.883 and 0.117, respectively. This means that we should consider the pressure gradient force, as well as the optical gradient force, in order to describe the SRG formation more reasonably. That is, SRG formation is mainly due to the optical gradient force, but we should also consider the volume change effect caused by the photoisomerization process.

#### IV. CONCLUSION

In conclusion, surface relief gratings on an Azo polymer film were observed and analyzed. We prepared a novel experimental procedure to examine the validities of

existing models, the optical gradient force model and the pressure gradient force model, for a complete set of linear polarization combinations. The heights of the SRGs at various polarization combinations of two writing beams could be explained well by a combined model of the optical gradient force model and the pressure gradient force model. As a result, we should consider the pressure gradient force, as well as the optical gradient force, in order to describe the SRG formation more reasonably.

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