Appl. Phys. B 72, 425–427 (2001) / Digital Object Identifier (DOI) 10.1007/s003400100531

Applied Physics B
Lasers
and Optics

Surface relief gratings in photoaddressable polymers generated by cw holography

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Received: 11 September 2000/Revised version: 5 December 2000/Published online: 21 February 2001 –

Abstract. Surface relief gratings (SRGs) are a widely observed phenomenon in holographic experiments with photoaddressable polymers. This article proposes a model which is able to explain the observed effects in cw experiments. It is based on forces in an electrical field which are caused by the inhomogeneous spatial distribution of the refractive index and the permittivity in the illuminated sample.

PACS: 78.66.Qn; 77.22.Ch

Photoaddressable polymers, which are described in a lot of articles not only due to their possible application as data storage media [1, 2], are azobenzene side-chain polymers in which the side chains are able to interact with a polarized light field. This interaction leads to a reorientation of the side chains perpendicular to the polarization of the light field and consequently to an increasing order parameter in the illuminated areas. Thus the refractive index of the material in aligned areas of the sample is different from that in dark areas. Though these substances are well investigated, some phenomena such as the appearance of surface relief gratings (SRGs) are not completely understood. In 1995 two groups [3, 4] reported on SRGs in holographic experiments with cw lasers, and in 1999 Ramanujam [5] found SRGs in pulsed experiments with azobenzene copolymers. Even in oxide materials SRGs were found due to the coupling of the piezoelectric constant with a space charge field as reported by Pankrath [6]. The gradient force model set up by Tripathy et al. [7], the mean field theory by Hvilsted et al. [8], other theories that consider free volume changes and pressure gradients [9, 10], and optically controlled anisotropic models [11] only partially explain the observed effects. Any theory which claims to explain the observed effects has to take the strong dependence on the light polarization into account. A complete discussion of all of the proposed models is given by Viswanathan et al. [12], who favor the gradient force model. However, we developed a more general approach.

In most of the described experiments holographic gratings such as intensity gratings or phase gratings are applied. Holographic intensity gratings arise from two parallel polarized writing beams when they are superimposed. The light intensity varies spatially from regions of complete darkness to maximum intensity, as depicted in Fig. 1. However, when we superimpose writing beams which are perpendicularly polarized, we observe holographic phase gratings. When vertically and horizontally polarized beams are superimposed, the polarization of the light changes from a $+45°$ angle with respect to the x_2-axis through elliptical to $-45°$ angle with respect to the x_2-axis and backwards to the $+45°$ direction as shown in Fig. 2. In this paper a model is proposed which describes SRGs in photoaddressable polymers caused by intensity and phase gratings. The idea behind the theory for the cw-generated SRGs is similar to that for SRGs generated by a pulse laser, as published previously [13] and is based on the fact that the permittivity of the sample is modulated due to the periodic alignment of the polymer side-chains. In contrast to the gradient force model, which takes electrical polarization effects to be responsible for SRGs, we assume that gradients of permittivity result in a force density if an electrical field is applied. This force density causes the modulations of the surface.

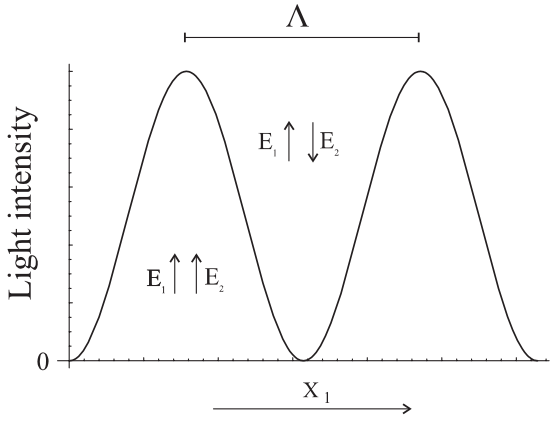

Fig. 1. Light intensity distribution in the x_1 direction in an intensity grating. Λ is the grating parameter

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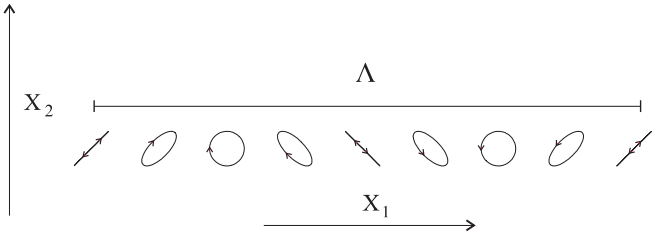

Fig. 2. Polarization state in the x_1 direction in a phase grating formed through one vertically and one horizontally polarized writing beam. Λ is the grating period

1 SRGs in intensity gratings

We begin our calculation at the time when the incident holographic intensity grating has generated a refractive index modulation of maximum value in the sample, the latter being in temporal equilibrium. In fact it was observed that a refractive index modulation often precedes the generation of SRGs [9, 14, 15]. Zilker et al. reported light-induced refractive-index variations of about $\Delta n = 0.1$ [16], but higher values seem to be achievable. Further, we suppose that there is no permanent polarization in the sample. That can be assumed because, although the dipole-moment carrying side chains are aligned parallel, their free ends point randomly in opposite directions.

The permittivity can be calculated using the formula

$$n = \sqrt{\varepsilon\mu}, \tag{1}$$

in which ε is the permittivity and μ the magnetic permeability. In the investigated polymers the magnetic permeability can be set to $\mu = 1$. The modulated refractive index n and permittivity ε are shown together with the light intensity in arbitrary units in Fig. 3. The permittivity varies by about 20% when the refractive index is modulated by $\Delta n = 0.1$.

If we generalize (1) for anisotropic, diamagnetic media, we obtain

$$\widetilde{\varepsilon} = \widetilde{n}\,\widetilde{n}\,, \tag{2}$$

where $\widetilde{\varepsilon}$ and $\widetilde{n}$ represent the corresponding tensors. In holographic gratings the refractive index and the permittivity are to the first order modulated along the grating vector (x_1-axis), while they are constant along the x_2- and x_3-axes. That allows us to give the permittivity tensor the following form:

$$\begin{pmatrix} \varepsilon_1(x_1) & 0 & 0 \\ 0 & \varepsilon_2(x_1) & 0 \\ 0 & 0 & \varepsilon_3(x_1) \end{pmatrix}. \tag{3}$$

In contrast to the light intensity the polarization of the incident light is constant over the whole illuminated area when intensity gratings are applied. Due to that fact we are able to simplify our calculations, since all components of the electric field vector except one vanish. Without loss of generality, we assume furthermore that the light is polarized in the x_2 direction and the electrical field vector is only dependent on the x_1-axis.

The general electric force density, which is exerted by electromagnetic fields on matter, is when neglecting the magnetic term [17]

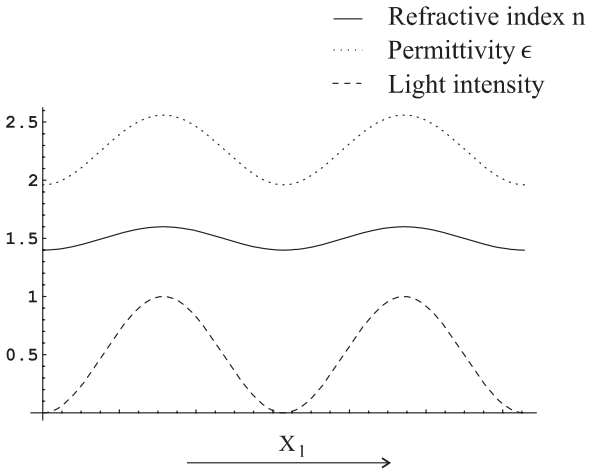

Fig. 3. Refractive index n and the dielectric constant ε formed by an intensity grating in the x_1 direction

$$f_\alpha = \frac{1}{2}(\boldsymbol{D}\boldsymbol{E}_{,\alpha} - \boldsymbol{E}\boldsymbol{D}_{,\alpha}), \tag{4}$$

where the comma in the index denotes the partial derivative with respect to the corresponding coordinate. The electric displacement is calculated as

$$\boldsymbol{D} = \varepsilon_0\widetilde{\varepsilon}\boldsymbol{E} \tag{5}$$

and, in particular,

$$\boldsymbol{D} = \varepsilon_0 \begin{pmatrix} 0 \\ \varepsilon_2(x_1)E_2(x_1) \\ 0 \end{pmatrix}. \tag{6}$$

We insert this result into (4) and obtain, when we apply the product rule, a force density along the x_1-axis given by

$$f_1 = -\frac{1}{2}\varepsilon_0 E_2^2(x_1)\frac{\partial}{\partial x_1}\,\varepsilon_2(x_1). \tag{7}$$

When the incident light is polarized along the x_1-axis, we get

$$f_1 = -\frac{1}{2}\varepsilon_0 E_1^2(x_1)\frac{\partial}{\partial x_1}\,\varepsilon_1(x_1); \tag{8}$$

the components f_2 and f_3 of the force density vanish in both cases. We approximate the permittivity ε_1 or ε_2 respectively with a sinusoidal function

$$\varepsilon_{1,2}(x_1) = \varepsilon_0' + \Delta\varepsilon_{1,2}\,\sin\left(\frac{2\pi}{\Lambda}x_1\right), \tag{9}$$

with a constant share ε_0', which is modulated with an amplitude of $\Delta\varepsilon_{1,2}$ and periodicity given by the grating parameter Λ. The incident light field of the intensity grating is a standing wave. Therefore the components E_1 or E_2 of the electric field vector can be set to

$$E_{1,2} = E_{1,2}'\sin\omega t\,\sin\frac{\pi}{\Lambda}x_1, \tag{10}$$

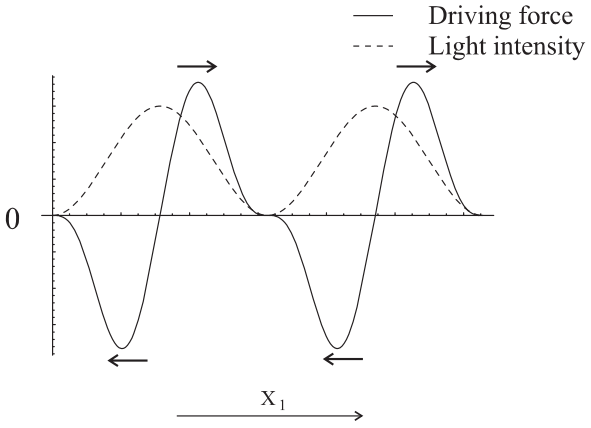

Fig. 4. x_1 component of force under a periodical modulation of the incident light. The material is pulled out of areas with high gradients of the permittivity (*arrows* denote the force direction)

where ω is the angular velocity of the writing beam, $E'_{1,2}$ the amplitudes of the light field and Λ the grating parameter.

Figure 4 shows the sinusoidal intensity distribution caused by the grating, which corresponds to the factors E_1^2 and E_2^2 in (7) or (8), respectively. The amplitude of the resulting force density in the x_1 direction is calculated by inserting (10) and (9) in (7) and is depicted in Fig. 4 in arbitrary units. The force density does not depend on the direction of the incident electric field vector; in the first half-period of the intensity modulation it points towards the negative x_1-direction, and in the second half towards the positive x_1-direction (arrows in Fig. 4). We discover a periodically time-dependent force density with magnitude and direction dependent on the x_1 coordinate, which pulls the material out of areas with high gradients of permittivity. To explain gain effects [16], which occur when the writing beams are switched off, we assume that the SRGs are formed under the electrical field of the reading beam. Due to our general set-up the described force density has first-order magnitude.

The trans-cis cycles of the azo-groups seem still to be necessary not only for aligning the side chains but also to soften the material as recently shown by Neher et al. [18].

2 SRGs in phase gratings

The theory developed for intensity gratings can be in principle applied to phase gratings. Therefore we want to outline some arguments. The polarization-induced anisotropic orientation of the side chains leads to an inhomogeneous distribution of the refractive index and the permittivity along the grating vector. These variables vary with the same periodicity as the polarization of the phase grating and the SRG, respectively. Thus a periodical force density is generated.

The fact that the largest SRGs occur under circularly polarized beams, as reported by [10], can be easily explained by the strong modulation of the permittivity under this geometry. Although the principle of calculation is similar, the varying light polarization of the incident phase grating and the non-vanishing components of the electric field vector prevent some of the simplifications made above. Nevertheless it is easy to recognize that our model is able to explain the observed SRGs so far in a qualitative way. A theoretical calculation of SRGs generated by phase gratings has to consider the described tensor property of the permittivity and the varying polarization of the light field.

3 Conclusions

The model is able to explain the structures which are observed in the experiments with azobenzenes. It predicts that generally internal stress appears in samples with a varying refractive index if an electric field is applied. Whether it is important that the field is an oscillating light field or whether a static electrical field will show similar effects has to be clarified in further experiments. Nevertheless it has to be pointed out that a varying refractive index exists in the sample when we start our consideration. Whether this variation is caused by a holographic grating or whether it is caused by other sources plays no role for the resulting force density. Although the principle of generating SRGs under cw conditions is similar to the theory for SRGs written with pulsed lasers [13], there are still some essential differences. Under pulse conditions the modulation of the refractive index and the permittivity is caused by local thermal heating as a result of intensity gratings. Due to the constant temperature distribution when phase gratings were applies, we observed no SRGs in our pulsed experiments [13]. The softening of the material is achieved thermally, and trans-cis cycles of the side chains, and therefore chromophore reorientation, play a negligible role [13]. Indeed we found pulse-generated SRGs in materials without any azo-functionality.

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