XXVI ENFMC *- Annals of Optics* *Volume5 - 2003*

Holographic Techniques to Study Reaction Kinetics in Photosensitive Materials

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Abstract

We use a phase-modulated two-wave mixing experiment with simultaneous measurement in both transmitted beams directions to study photoreaction kinetics in the positive photoresist AZ1518 (novolak-diazoquinone). From the processed two-wave mixing signals we obtained the real time evolution of the refractive index and absorption coefficient, which were compared with independent measurements. To obtain the kinetic constants from the temporal evolution of the optical constants, a model of two chain photosensitive reactions was developed.

Introduction

Holographic techniques have been successfully employed to study photosensitive materials because they ally the high sensitivity of the diffraction measurement, the high spatial frequency possibilities of the interference pattern and the ability to detect dynamic gratings [1]. The use of phase-modulated two-wave mixing experiments and synchronous detection improve these techniques providing higher sensitivity and phase sensitive detection [2].
In 1985/86 this phase-modulated two-wave mixing technique was improved by measuring both first and second harmonics in both directions of the transmitted beams. This procedure permits to separate the signals of the phase to the amplitude gratings [3]. However, the phase perturbations in the holographic setup are not compensated neither controlled. This mean that the fringe contrast is not kept constant during the exposure. About the same years it was proposed the detection of the first and second harmonics of the wave mixed signal, but with the aim to detect and to correct phase perturbations during the holographic recording [2]. In these experiments it was assumed that the amplitude modulation was negligible in the photosensitive material. In a later paper [4] it was proposed the measurement of the two-wave-mixing signal in both directions of the transmitted beams, to select and to stabilize the photorefractive or the photochromic grating in photorefractive crystals.

In this paper we use this technique [4] to study the recording process and the kinetics of light induced reaction in a commercial positive photoresist films of the series AZ 1518.

The Method of Measurement

The technique is based in the exposition of the photoresist film to an interference pattern, produced by the incidence of two plane coherent waves (A and B). This pattern generates a real time grating in the material that self diffracts the incident waves. If the modulation is low, this real time grating can be analyzed as two uncoupled gratings formed by the refractive index and the absorption coefficient modulations of the film.
If the modulation is low and the film is thick enough, the Coupled Wave Theory [5] can be used to calculate the diffracted waves for a mixed phase and amplitude grating. In this case, the first diffracted order A_{+1} is given by:

$$A_{+1} = -D\left[\frac{\Delta\alpha \cdot d}{4\cos\theta_0} + i\,\frac{\Delta n \cdot \pi d}{2\lambda\cos\theta_0}\right]A \tag{1}$$

Being *A* the amplitude of the incident wave, Δn the peak to peak modulation of refractive index, $\Delta\alpha$ the peak to peak modulation of the absorption constant, *D* the average attenuation of the wave, d the grating thickness and λ the incident wavelength.
As it can be seen, from the right side of equation (1), the contribution of the Δn and $\Delta\alpha$ are $\pi/2$ phase shifted ('i' term). This phase shift is the key of the diffraction grating separation method [6]. Analyzing the interference between each transmitted beam and the diffraction of the other beam, in both directions of the transmitted beams, this term results in a symmetric contribution from the amplitude grating (absorption coefficient modulation) and an anti-symmetric contribution from the phase grating (refractive index modulation). Thus, adding and

subtracting the voltage signals that are proportional to light intensity in each directions of the transmitted beams (V_A and V_B), it is possible to obtain a signal proportional only to the phase or to the amplitude grating [6]. Equations (2.1) and (2.2) resumes such dependence of the signals.

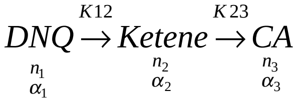
$$[V_A + V_B] \sim \sqrt{\eta_{1A}} \sim \frac{\Delta\alpha \cdot d}{4\cos\theta_0} \tag{2.1}$$

$$[V_A - V_B] \sim \sqrt{\eta_{1P}} \sim \frac{\Delta n \cdot \pi d}{2\lambda \cos\theta_0} \tag{2.2}$$

With η_{1A} and η_{1P} being the diffraction efficiencies of the amplitude and phase grating respectively.

The Photoresist Reaction Kinetics

The positive photoresists of the AZ series are composed of a base resin (novolak), a photoactive inhibitor (diazoquinone=DNQ) and a suitable solvent [7]. Radiant energy at proper wavelength destroys the inhibitor, being the reaction velocity (K_{12}) proportional to the light intensity. The DNQ loose molecular nitrogen and go to a ketene. This ketene can be hydrated in a reaction light independent (velocity K_{23}), going to a carboxylic acid (CA) [7]. This chain reaction can be expressed as:



$$\underset{\substack{n_1\\ \alpha_1}}{DNQ} \xrightarrow{K12} \underset{\substack{n_2\\ \alpha_2}}{Ketene} \xrightarrow{K23} \underset{\substack{n_3\\ \alpha_3}}{CA}$$

These two reactions change microscopically the concentrations of these specimens, changing the film chemical composition, and leaving to a temporal macroscopically change in the refractive index and absorption coefficient of the film. We suppose in our model that the base resin (novolak) is kept unaltered during this process.

Defining n_1 and α_1 as the molecular polarizability and the molecular absorptivity of the DNQ respectively, n_2 and α_2 the same for the ketene and n_3 and α_3 of the CA, the macroscopic refractive index and absorption coefficient of the mixture of specimens can be represented by:

$$\alpha = \sum_{i=0}^{3} \alpha_i m_i$$

$$n = \sum_{i=0}^{3} n_i m_i$$

and (3)

With m_i being the molecular concentration of each species (i=1: DNQ; i=2: kenete; i=3: CA; i=0: base resin)

Using a simple kinetic model to describe the temporal evolution of the concentrations m_i in equation (3), we can found that the macroscopic changes in the film absorption constant and refractive index is given by:

$$\Delta\alpha = P_1 \cdot e^{-P_2\cdot(1-m)\cdot t} + P_4 \cdot e^{-P_2\cdot(1+m)\cdot t} - (P_1 + P_4)\cdot e^{-P_5 \cdot t}$$

(4)

$$\Delta n = P_1' \cdot e^{-P_2\cdot(1-m)\cdot t} + P_4' \cdot e^{-P_2\cdot(1+m)\cdot t} - (P_1' + P_4')\cdot e^{-P_5 \cdot t}$$

(5)

Being m = fringe contrast; $P_2 = K_{12}I_0$; $P_5 = K_{23}$ (the kinetic constant of the second reaction); P_1 and P_4 are functions of K_{12}, K_{23}, α_1, α_2 and α_3) and P_1 and P_4' are functions of K_{12}, K_{23}, n_1, n_2 and n_3).

Experiment and Results

The Positive AZ-1518 (from Hoechst) photoresist films were spin coated resulting in a 4.0µm thick photoresist film on glass substrates. The samples were exposed in a holographic setup using the line 457.9 nm of an Argon laser. Figure 1 shows the evolution of Δn and Δα obtained from the experimental measurements of the signals represented by Eq. (2.1) and Eq. (2.2), as a function of the exposure time of the photoresist film to an interference pattern of 0.46 µm of period. Note that Δn corresponds to the variations of the refractive index from the dark to the bright fringe and the same occurs for the absorption constant Δα. As it can be seen, when the exposure time increases, Δn and Δα signals also increase. These modulations reach certain maximum values and then decrease. This decreasing can be explained by the fact that the light pattern is not binary but sinusoidal. Thus, when the middle of the bright fringe reaches the saturation, the surrounding areas continue to be exposed, increasing the saturated areas until the whole material became saturated.

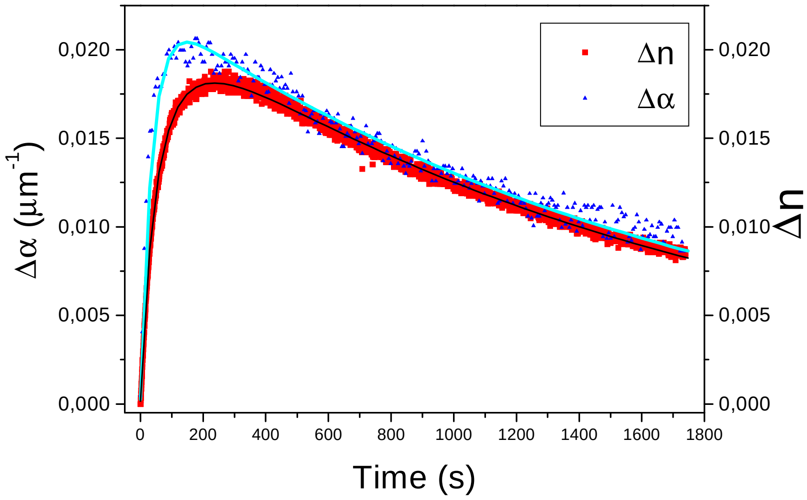


Figure1. Δn and Δα temporal evolution obtained from the diffraction measurements (at λ= 458nm) with their respective fittings to Eq. (5) and Eq. (6) respectively.

As it can be observed in Figure 1 the Δα evolution is faster than the Δn evolution, and the same behavior occurs for all measured samples. As the efficiency of the amplitude grating is of about 100 times smaller than that of the phase grating, the Δα measurements are noisier. Due this fact when we try to fit the Δα curve to Equation 4 (which has four free parameters) the fitting is very critical and it furnishes values for K_{12} and K_{23} different than those obtained from the fitting of Δn to Equation 5.

In order to reduce the number of parameters in the Δα fitting and considering the different growing rates of the measurements, we assume that the three species (DNQ, ketene and CA) have different molecular polarizability (n_1, n_2 and n_3 respectively) but that their molecular absorptivity (α_1, α_2 and α_3) change only in the first reaction photosensitive reaction (thus we assume that $\alpha_3=\alpha_2$). This is justified because only the first reaction is photosensitive. This reduces equation 4 to a model of a single reaction:

$$\Delta\alpha = P_1 \cdot e^{-P_2 \cdot t} \cdot Sinh\left[P_2 \cdot m \cdot t\right] \qquad (6)$$

By fitting the equations (5) and (6) to the experimental data we found a value of 0.0031 cm^2/mJ for K_{12} from the Δα data and 0.0032 cm^2/mJ from the Δn data. From the Δn data it is possible also to find the second reaction kinetic constant (K_{23}) whose value is 0.01s^{-1}.

Independent measurements of the refractive index and absorption coefficient of several samples, exposed at different homogeneous doses, at the same wavelength λ=458nm, are show in **Figure 2**, as a function of the exposure energy.

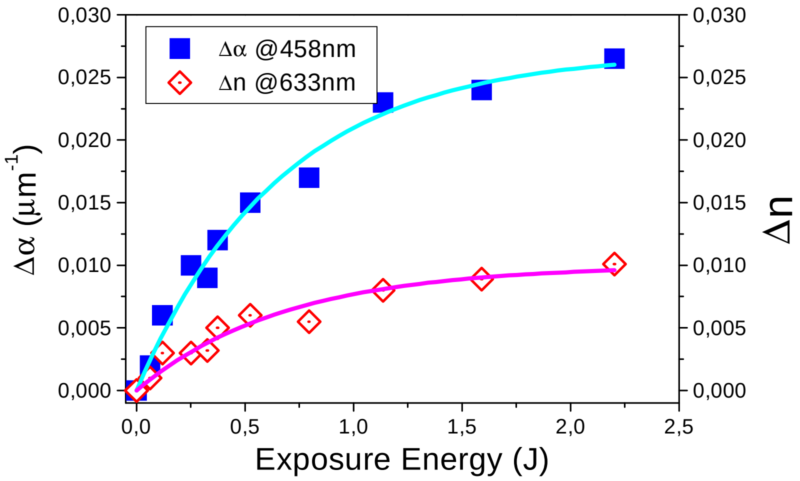


Figure2. Independent Δn and $\Delta\alpha$ temporal evolution measurements

The refractive index measurements were performed using the m-line technique at the wavelength 633nm. The refractive index difference, between the photoresist bleached and unbleached, at λ=458nm, was measured by the Abelès Method [9], resulting a value of Δn=0.027. The absorption coefficient was measured at 458nm, through transmittance measurements, using a λ-9 spectrophotometer. From these curves it is possible just to find the K_{12} kinetic constant because the intermediary specie (ketene) is not detected (we consider it has enough time to be transformed in the final product CA). The fittings results in K_{12} value 0.0015 ± 0.0002 cm^2/mJ for the $\Delta\alpha$, and 0.0015 ± 0.0003 for the Δn.

Conclusions

The direct look of the temporal evolution of the signals Δn and $\Delta\alpha$ (figure 1) reveals that they have different time constants, that is an indicative of a more complex phenomenon than a single-reaction proposed by Dill [8]. A model of two chain reactions was developed to take into account such difference. The numerical values of the kinetic constants (K_{12}) obtained by the fitting of the curve of Δn to Eq. (5) and of $\Delta\alpha$ to Eq.(6) shown a good accordance, demonstrating the reasonability of the approach $\alpha_2=\alpha_3$.

Besides this fact, the maximum values of $\Delta\alpha$(= 0.025μm^{-1}) and of Δn(=0.027), between the photoresist bleached and unbleached, obtained from independent measurements at λ=458nm, are close than the maximum values shown in Figure1, demonstrating the ability of the method to perform quantitative measurements of the material optical constant changes. The maximum values of $\Delta\alpha$ and Δn of the curves in Figure 1 are smaller than those obtained from the independent measurements. This occurs because, due to the sinusoidal interference pattern, the complete bleached-unbleached situation is not fulfilled.

By the other side, the values of K_{12} obtained from Δn and $\Delta\alpha$ independent measurements (Figure 2), agree between themselves, but they differ significantly (about a factor 2) from those calculated from the diffraction measurements. This difference could be generated by other dynamical effect not considered in our model.

Although the applied model is not complete, the results demonstrate the possibilities of the method to study dynamical process in photoresist as, for example, the detection of intermediate products or secondary reactions that cannot be performed in an equilibrium physicochemical-situation

Acknowledgements

We acknowledge **Dr. Arnost Reiser** from Polytechnic University-USA for helpful discussion about the positive photoresist kinetics and **FAPESP** - Fundação de Amparo à Pesquisa do Estado de São Paulo (process 98/15.851-4) and **CNPq** - Conselho Nacional de Desenvolvimento Científico e Tecnológico for the financial support to this work

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