Analysis of a phase-modulating recording mechanism in negative photoresist

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We describe a process that produces an index-of-refraction modulation requiring no wet development. A negative photoresist, which is currently employed as a surface-modulating material in high-resolution photolithography, was used. This process may be useful in real-time optical recording. It could eventually be shown to be responsible for defects in high-resolution photolithography.

1. INTRODUCTION

Optical applications of photoresists in optical-component fabrication and as recording materials have been studied extensively. Photoresists exhibit some interesting properties that make them potentially useful: low noise, possibility of a linear response range,[1–3] and all the advantages of acting as a phase material. However, their limited wavelength range of response and low sensitivity have restricted their commercial applications almost exclusively to photolithography. Photopolymers do exist that need no chemical development[2–6]; this represents a considerable advantage over conventional silver halide films. A number of efforts were made and are in progress that are aimed at improving their spectral range and energy sensitivity.[7–11] A meeting was held[12] to discuss the state of affairs of nonclassical recording materials with special emphasis on photoresists, their mechanisms, and photosensitization procedures. Photoresists, and photochromic materials in general, have been thoroughly described from a phenomenological point of view, and a number of mathematical models have been proposed.[13–17]

In the present paper we describe a new process that we call negative photoresist heat development (NPHD). It results in an index-of-refraction modulation of a commercial negative photoresist that is currently used as a surface- (relief-) modulation material in photolithography. Once the NPHD process is finished, the photoresist may still be wet developed in the usual way, if desired, to produce a surface modulation too. The NPHD process is performed quite rapidly at moderate temperatures and requires no wet development. Hence it may be potentially interesting for real-time recording, optical correlation, and real-time interferometric holography. It may also be useful for Fourier synthesis in which the NPHD process would be required to superimpose precisely the multiple spatial components during exposure[18]; after that, a final wet development would be carried out. In high-resolution photolithography, the NPHD effect may be responsible for serious defects, as is briefly explained in Section 4. C.

Description of the Process

We found that, when a film of KMR 747 (a negative commercial Kodak photoresist) is exposed to light and subsequently kept at a moderate temperature (40–60°C), an index-of-refraction modulation appears without any wet development. The rapidity of this process increases strongly with temperature and does not depend on the spatial frequency of the recorded signal. No significant surface or absorption modulations were observed. After the NPHD process, the film may still be developed in the classical wet way to obtain the usual surface modulation. We have noted that the two types of phase modulation have opposite signs (see Section 3. A).

2. EXPERIMENTAL METHOD

We studied the Kodak KMR 747 photoresist film by recording a sinusoidal interference fringe pattern on it. We followed the time evolution of the diffracted light through the film while it was kept at a fixed temperature. This method presents some advantages, such as the possibility of large variations of the recorded spatial frequency and the possibility of measuring far from the low spatial frequencies, where noise predominates as a result of the nonuniformities, dust, and scratches that are on all optical interfaces.

A. Sample Preparation

Our film was prepared, as has been described in former papers,[19] by using a rolling machine. After being coated on a 1.5-mm-thick glass plate substrate, it was dried on a hot plate first and then drying was finished in an oven at 50–60°C for 1 or 2 h. When low-irradiance exposure was used, the sample was kept in a N_2 atmosphere for 1 or 2 h before being exposed; this increased its sensitivity by diffusing away the deactivating O_2 gas.[20] The photoresist film need not be carefully prepared because all noise arising from defects is of a low nondetected spatial frequency. Films were 1–2 μm thick.

The glass-coated film was positioned as a window in a specially made chamber.[21] Its temperature was regulated, and a stream of N_2 was sometimes passed through. The introduction of additional optical interfaces does not affect the measurement, as was explained above.

B. Exposure Setup

In Fig. 1 the experimental setup is shown. The 456-nm line of an argon-ion laser was used to project an interference fringe
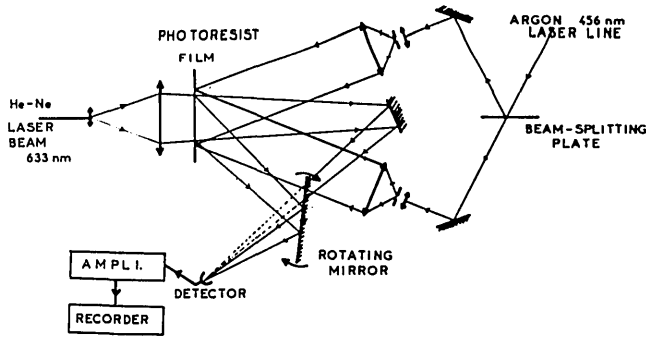
Fig. 1. Experimental setup. The setup used to record interference fringes on the photoresist film and the setup used to measure the diffraction spectrum are shown. The polarization rotator and the system employed to attenuate the intensity of the zeroth diffraction order are omitted. The latter permits measurement of low optical modulations using simple electronics.

pattern on the film. A polarization rotator sets the correct beam polarization, and a variable-transmittance metallic beam-splitter plate permits simultaneous splitting and intensity matching of both interfering beams. Because of all interfaces encountered by both beams, depolarizing effects must be correct[22,23] for reasonable contrast fringes to be obtained. Time exposures of about 5 min, totaling 0.5-J/cm² energy density, were used. This photoresist has low sensitivity at the wavelength we used, but we did not use longer exposures because of lack of confidence in the mechanical stability of our setup. The experimental setup is supported on a 200-cm × 100-cm × 10-cm granite bench on a massive wooden table standing on a sand base. A foamy antivibrating board is placed between the granite and the wood.

C. Measurement Setup

The measurement setup is also shown in Fig. 1. Using a 6328-Å He–Ne laser and a 500-nm focal-length lens, we measure the first-order-to-zero-order diffraction intensity ratio (I_1/I_0). We follow the evolution of this ratio as a periodic optical modulation develops in the film. A fixed mirror reflects the zero-order beam onto a fixed detector: a rotating mirror interrupts it periodically, directing the first-order beam onto the detector, thus permitting alternate measurements of both orders. Two crossed polarizers were used to attenuate the intensity of the zero-order beam, thus facilitating comparison of both orders.

Ratios I_1/I_0 as small as 10^{-6} were measured, corresponding to an optical phase modulation[24] of

$$x \equiv \frac{2\pi}{\lambda} \Delta(ne) = 4 \times 10^{-3} \text{ rad,} \tag{1}$$

where λ and $\Delta(ne)$ are the 6328-Å He–Ne laser wavelength and the peak-to-peak difference in film optical thickness for a sinusoidal phase modulation, respectively.

3. EXPERIMENTAL RESULTS

A. Optical Modulation of the Photoresist Film

Liquid gate techniques and other experimental data showed that there is neither a surface-modulation nor an absorption-coefficient variation of any relevance appearing as a

consequence of the NPHD process. Consequently, we accept an index-of-refraction modulation as the main recording mechanism involved. In fact, an absorption-coefficient modulation cannot be responsible for the observed diffraction since that coefficient remains negligibly small (less than 0.01 μm^{-1} for 0.5 $\mu m < \lambda < 0.7$ μm) during the NPHD process. Additional support for this hypothesis is provided by Fig. 2, which shows a linear relationship between measured values for the phase modulation x and the wave number $1/\lambda$. This linearity is predicted by Eq. (1) if the influence of chromatic dispersion on optical path change $\Delta(ne)$ is neglected.

We proved the absence of surface modulation by NPHD processing two samples and index matching them with the same commercial liquid resist solution ($n_D = 1.50$). The phase modulations were measured before (x) and after matching (x_G). In the presence of a perceptible surface modulation Δe, we can write explicitly

$$x = \frac{2\pi}{\lambda} \Delta e (n_R - 1), \tag{2}$$

$$x_G = \frac{2\pi}{\lambda} \Delta e (n_R - n_G). \tag{3}$$

Here n_R and n_G are the refractive indices of the solid resist film and the gating liquid, respectively. Substituting the experimental values $(n_R)_D = 1.54 \pm 0.03$ and $(n_G)_D = 1.50$ into Eqs. (2) and (3), we obtain

$$x/x_G \cong 13.$$

However, the above ratio was found to be 1.0 ± 0.1 when measured at $\lambda = 6328$ Å, thus showing the absence of any relevant surface modulation.

All experimental data consistently show that the recording mechanism for our NPHD process is based mainly on an index-of-refraction modulation, so Eq. (1) can be better written as

$$x = \frac{2\pi}{\lambda} e \Delta n. \tag{4}$$

We have independently measured a 0.4% decrease in the photoresist index of refraction when the film is exposed to a uniform illumination and then NPHD processed. This means that NPHD modulation is opposite in sign to the usual surface wet-development modulation.
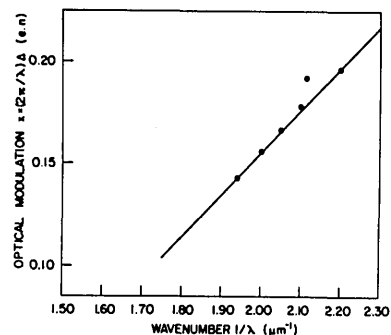

Fig. 2. For some selected samples, the ratios I_1/I_0 were measured for different wavelengths λ; the optical phase modulations were calculated through Eq. (5) and plotted against $1/\lambda$. The good linear relation shown means that the measured optical modulation is actually a phase modulation as described by Eq. (1).
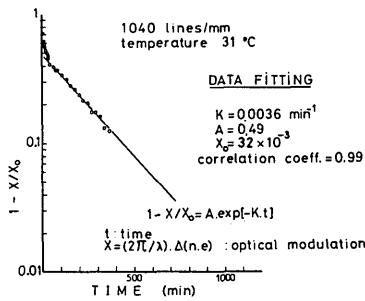
Fig. 3. Experimental data fitting. The good fit with Eq. (6) shown is numerically represented by the high correlation coefficient (0.99). Some more experimental data and their calculated parameters appear in Table 1.
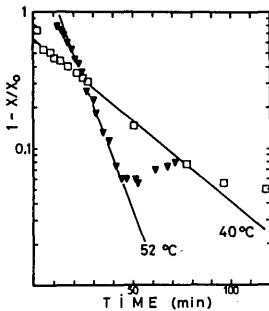

Fig. 4. Experimental data and their best fit to Eq. (6) are shown for different spatial frequencies of the registered signal. Triangles are data for 238 lines/mm and 52°C, and squares are data for 875 lines/mm and 40°C. It is seen that the increase of sample temperature also accelerates the decay process.
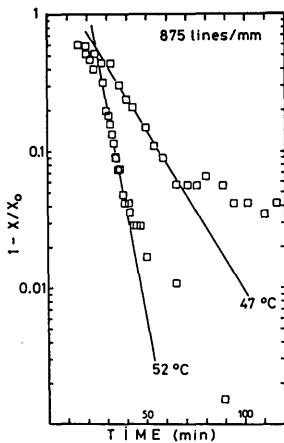

Fig. 5. Experimental data and their best fit to Eq. (6) are shown for the same spatial frequency of the registered signal (875 lines/mm) and different temperatures. The time constant K in Eq. (6) (represented by the slope of the curves) increases with temperature as shown.

The above reasons lead us to select the parameter x, as defined by Eq. (4), to characterize the change in optical structure of the film during the NPHD process. Accordingly, we express the experimental I_1/I_0 ratios in terms of this parameter by using the relation[24]

$$I_1/I_0 = \left[\frac{J_1(x/2)}{J_0(x/2)}\right]^2 , \qquad (5)$$

where J_i is the ith-order Bessel function.

In doing this we had to suppose that our film exhibits a strictly sinusoidal phase modulation. This fact is easily accepted because the photoresist behaves rather linearly[16] for the low modulation values involved.

B. Temporal Evolution of the Negative Photoresist Heat Development Process in KMR 747

The time evolution of the x variable [Eq. (4)] fits an exponential law reasonably well:

$$x = x_0[1 - A \exp(-K \times t)],$$

$$1 - \frac{x}{x_0} = A \exp(-K \times t), \qquad (6)$$

where x_0 is the limiting value for x, t is the time, and K is the time constant of the process. The coefficient A is related to the initial experimental conditions. Figure 3 illustrates the fit of the data with Eq. (6). Figures 4 and 5 also show good agreement with Eq. (6). The high values of the correlation coefficients appearing in Table 1 support the selection of that equation for describing our process. We remark that Eq. (6) may represent a mass-diffusion process,[25] a first-order chemical reaction,[26] or any other formally analogous phenomenon.

At the beginning of the process, the sample temperature is not quite stable yet, so the data depart from the theoretical curve; at the end of our run the data do not fit either, probably because of some secondary slow-decay process taking place (see Figs. 3–5). This decay appears to be more relevant the higher the temperature, as is seen in Fig. 4. For these reasons, the first points and the last ones (typically for $x > 0.9\,x_0$) are rejected for calculation purposes.

C. Temperature Influence on the Velocity of the Negative Photoresist Heat Development Process

The velocity of the NPHD process, as characterized by the time-constant parameter K in Eq. (6), is highly dependent on temperature, as is seen in Fig. 5. Figure 6 shows the dependence of K on the reciprocal absolute temperature of the sample for spatial frequencies varying from 238 to 1040 lines/mm. There can be seen no significant spatial-frequency dependence on this relation. Then we can write

$$K = a \times \exp(-b/T), \qquad (7)$$

where T is the absolute temperature and the experimentally obtained values for the parameters are $a = 3.13 \times 10^{28}$ min^{-1} and $b = 21971$ K.

D. Spatial-Frequency Influence on the Velocity of the Negative Photoresist Heat Development Process: A Non-Mass-Diffusion Process

The absence of any spatial-frequency dependence shows that no mass-diffusion effect can be at the base of our process.[25,27] The data in Fig. 6 are conclusive in this respect. We are thus led to believe that the NPHD process, although not fully understood, is related to local molecular-structure changes or chemical reactions concerning statistically stationary molecules. Any mass-diffusion mechanism should result in a square-law dependence on spatial frequency,[25,27] which is far from our experimental results. In a former paper[25] we erroneously considered the hypothesis of a mass-diffusion mechanism.

Table 1. Some Experimental Results[a]

Spatial Frequency (lines/mm)	Mean Temperature of Sample (°C)	Number of Experimental Points	Best-Fitting Parameters			
			Half Optical Modulation $[(x_0/2) \times 10^3]$	Time Constant $(K \times 10^3 \text{ min}^{-1})$	Coefficient (A)	Correlation Coefficient
970	22	45	18	0.10	0.53	0.92
238	29	25	16.2	0.92	0.86	0.99
380	30.5	19	8.9	0.574	0.52	0.98
380	31	9	19.4	0.838	0.69	0.99
720	31	36	12	0.426	0.56	0.97
1040	31	14	16.0	3.61	0.49	0.99
238	32.5	16	11.8	3.1	0.99	0.99
806	36	31	14.7	2.01	0.55	0.90
238	39	35	35.5	3.2	0.87	0.99
1040	40	10	11.5	33.25	1.08	0.98
805	40.5	17	20.2	14	0.93	0.97
875	·40.5	10	18	27.5	0.64	0.99
1040	42	7	13.7	28.7	0.89	0.97
1040	42	6	13.6	30.21	0.94	0.97
238	44	13	21.8	23.5	0.97	0.99
875	47	8	12.95	54.5	2.2	0.99
875	48	5	11.2	86	1.57	0.99
875	52	10	16.17	180	47.0	0.98

a In this table are shown some 18 selected experimental results. Three among these are shown graphically in Figs. 3–5. The experimental points are fitted to Eq. (6) looking for a maximum value for the correlation coefficient; then the parameters $x_0/2$, A, and K are noted. The coefficient A depends largely on the choice of experimental time origin, which did not not necessarily correspond with the time origin in Eq. (6). The primary experimental data are the I_1/I_0 ratios as reported. These data are transformed into half optical modulation $x/2$ through Eq. (5). The latter data are processed in the form described above.
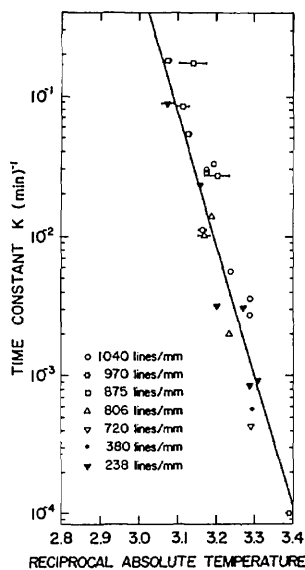

Fig. 6. Experimentally obtained time constant K plotted against the reciprocal absolute temperature. The values of K are obtained by linear fitting of Eq. (6) as shown in Fig. 3. The relation shown in Eq. (7) is obtained from these data and plotted as a continuous line. It is seen that there is no noticeable influence of the spatial frequency of the signal on that relation.

4. SOME RELEVANT DERIVATIONS

A. KMR 747 Photoresist Utilization as a Real-Time Recording Material

The NPHD process does not require any wet development, and its speed is highly dependent on temperature. We propose to use it as a real-time recording material, the meaning

Table 2. Performance of KMR-747 Photoresist as a Real-Time Recording Material[a]

Temperature (°C)	K (min⁻¹)	Time for Reaching 90% of Final Modulation
20	8.5×10^{-5}	27000 min
30	1×10^{-3}	2300 min
40	1×10^{-2}	230 min
50	0.1	23 min
60	0.69	3.3 min
70	4.75	0.5 min
80	29.0	4.0 sec
100	820	0.2 sec

a $K = a \times \exp(-b/T)$; $a = 3.13 \times 10^{28} \text{ min}^{-1}$; $b = 21971$ K.

of this term depending on experimental conditions and user's necessities. Table 2 illustrates this fact: at room temperature this material self-develops slowly, but at 100°C it reaches 90% of its final modulation value in about 0.2 sec.

When using the NPHD process, care must be taken (1) to optimize the heating time, as there seems to exist a competitive, though slower, decay process that also increases with temperature, and (2) to keep the recorded information out of any active light because it is not fixed. No significant decay was observed after the sample had been kept in darkness at room temperature for some months. Direct exposure from a 0.5-mW He–Ne laser beam acting continuously for several days did not damage the sample either.

B. Index-of-Refraction and Molecular Changes: Activation Energy for an Unknown Process

Under certain conditions there is a linear relationship between the index-of-refraction modulation and the corresponding

molecular-concentration changes, thus permitting estimation of the activation energy for the unknown process involved. From the general relation[28]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \sum_i N_i a_i, \qquad (8)$$

relating the index of refraction n with the concentration N_i of a molecular specimen with polarizability a_i, and from Eq. (4), we obtain

$$x = \frac{2\pi}{\lambda} e \Delta n = Z \times \Delta a \times (N_{0j} - N_j) \qquad (9)$$

in the limit when $\Delta n/n \ll 1$. Here the parameter Z is defined as

$$Z \equiv \frac{4\pi^2}{9} \frac{e}{\lambda} \frac{(n^2 + 2)^2}{n}, \qquad $$

$\Delta a \equiv a_i - a_j$ is the change in polarizability for a molecule converting from the j to the i molecular specimen, and N_{0j} and N_j are the initial and present molecular concentrations of jth specimen. It follows that

$$dx = -Z \times \Delta a \times dN_j. \qquad (10)$$

For a first-order chemical reaction involving conversion of specimen j to i, we write[26]

$$dN_j = -k_a \times N_j \times dt, \qquad (11)$$

k_a being the velocity constant of the reaction. Differentiating Eq. (6), we have

$$dx = x_0 AK \exp(-Kt)dt, \qquad (12)$$

and, by combining Eqs. (12), (11), and (10), we conclude that

$$Z\Delta a k_a N_j = x_0 AK \exp(-Kt) \qquad (13)$$

and

$$Z\Delta a k_a N_j = (x_0 - x)K. \qquad (14)$$

From Eq. (9), we deduce that

$$x_0 - x = Z \times \Delta a N_j. \qquad (15)$$

After substituting Eq. (15) into Eq. (14), we get

$$k_a = K. \qquad (16)$$

This result enables us to identify the time constant K of our process with the rate constant k_a of the chemical reaction. We can evaluate the activation energy E_A for our NPHD process according to the well-known relation[26]

$$k_a = k_{a0} \exp(-E_A/RT). \qquad (17)$$

Comparing Eqs. (17) and (7), we see that

$$E_A = bR. \qquad (18)$$

This represents a value $E_A \simeq 43$ kcal/mol for our NPHD process. Attention is called to the fact that the value of k_{a0} derived from Eq. (7) is unrealistically higher than reported values for this parameter for a first-order chemical reaction.[26] In spite of this objection, this mechanism of reaction fits better than other simple hypotheses that we tried.

C. Source of Defects in High-Resolution Photolithography

The photoresist we studied is commercially used in high-resolution photolithography, namely, in microelectronics. During exposure this film is not supposed to change its optical properties significatively, thus remaining optically homogeneous and permitting good-quality recording. In this paper we show that relevant optical inhomogeneities (index variations) do appear during exposure. These inhomogeneities in turn will modify the light distribution inside the film, thus eventually leading to serious defects. The feedback effect of this scattering on the recording-field distribution has been described for photochromic materials already.[13,14,29] The relevance of this limitation in commercial photolithography is a point of technological importance and will be analyzed in a forthcoming paper.

5. CONCLUSIONS

We have reported a new process that should permit utilization of a negative commercial photoresist as a real-time irreversible recording material. This process can also be utilized for identifying or positioning the recorded data before development in the usual wet way.

Although the optical-modulation values actually involved in the present work are rather low, the process is potentially interesting for thicker films. For our reported 0.4% maximum-attainable index modulation, we would need a 100-μm-thick photoresist film to get a 2π optical phase modulation in the visible wavelength range.

It is also pointed out that this process may inadvertently be responsible for defects in high-resolution photolithography. The extent of this effect needs to be analyzed.

The speed of the process referred to is not dependent on the spatial frequency of the recorded signal but is strongly dependent on temperature. An index-of-refraction modulation seems to be the recording mechanism, and no mass diffusion is involved. Even though we do not know the full nature of this process, we evaluate its activation energy, hoping such an evaluation will help to gain a deeper insight into its chemical nature.

This research was carried out on a single particular commercial product, and the question arises whether our conclusions should be limited just to this material or extended to a class of negative resists.

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