Developed profile of holographically exposed photoresist gratings

Bernardo de A. Mello, Ivan F. da Costa, Carlos R. A. Lima, and Lucila Cescato

A simulation of the profile of holographically recorded structures in photoresists is performed. In addition to its simplicity this simulation can be used to take into account the effects that arise from exposure, photosensitization, development, and resolution of positive photoresists. We analyzed the effects of isotropy of wet development, nonlinearity of the photoresist response curve, background light, and standing waves produced by reflection at the film–substrate interface by using this simulation, and the results agree with the experimentally recorded profiles.

Key words: Holographic gratings, photoresist processing.

1. Introduction

Surface-relief structures holographically recorded in photoresist are a subject of great interest in optics and optoelectronics. For applications in holography for which the component is either directly recorded in photoresist or embossed for replication, a linear response is desired. In other applications such as photolithography, in which one can use the photoresist as a mask to etch a substrate, a strong nonlinear response is more adequate to obtain an etch-resistant square profile. In each case the precise control of a recorded profile in the photoresist is desirable.

Most applications of holographic recording in photoresist are concerned with the fabrication of optical components. The diffraction efficiency of such components is highly dependent on the profile of the diffracting structure, and some interesting components can be obtained if the profile can be constructed. The accurate control of a recorded profile in photoresists is therefore indispensable for producing diffraction components or devices.

The profile of recorded structures in photoresist depends on several factors; light exposure pattern, photoresist sensitization, and development. In such cases, simulations are useful tools to improve the understanding of the effects of each process parameter.

In this paper we develop a simulation that can be used to determine the final profile recorded in photoresist under holographic exposures, and we use this simulator to study the influence of some process parameters. The simulator incorporates a string development algorithm to describe the photoresist profile evolution, the development rate, that can be obtained either from experimental measurements or from the model of Mack, and a spatial frequency filter represented by a simple modulation transfer function.

2. Model

As is well known positive photoresists are basically composed of three components: a photoactive compound (inhibitor), a base resin, and a solvent. The base resin is soluble in aqueous alkaline developers and the presence of the photoactive compound strongly inhibits its dissolution. The light neutralizes the photosensitive compound and increases the solubility of the film. After development in such solutions an intensity light pattern is converted into a relief structure.

The resulting relief profile recorded in photoresist depends on both the exposure light pattern through the film and on the complete response of the photoresist, including the development. These processes can be mathematically described, and the profile in the photoresist can then be calculated.
2.A. Exposure Pattern
Neglecting multiple reflections, the holographic interference pattern that is inside the photoresist film, generated by the interference of two coherent beams and their respective reflections, can be represented by see Fig. 1
\[ I(x, z) = |E_1 \exp(ik_1 \cdot r) + E_2 \exp(ik_2 \cdot r)|^2 + E_{1r} \exp(ik_2 \cdot (d - r)) + E_{2r} \exp(ik_1 \cdot (d - r)) |^2, \]
where
\[ E_1 = E_1 \cdot \hat{y}, \quad E_{1r} = -E_{1r} \cdot \hat{y}, \]
\[ E_2 = E_2 \cdot \hat{y}, \quad E_{2r} = -E_{2r} \cdot \hat{y}, \]
\[ k_1 = 2\pi/\lambda_0[\cos \theta x + \sin \theta z + ikz/\cos \theta], \]
\[ k_2 = 2\pi/\lambda_0[-\cos \theta x + \sin \theta z + ikz/\cos \theta], \]
and \( \theta \) is equal to half of the angle formed between the two interfering beams inside the film, \( n \) is the real part of the photoresist refractive index, \( k \) is the imaginary part of the photoresist refractive index with \( \alpha = 4\pi k/\lambda_0 \) as the absorption coefficient, \( \hat{x}, \hat{y}, \) and \( \hat{z} \) are unit vectors in the direction of the \( x, y, \) and \( z \) axes, respectively.
\[ r = x\hat{x} + z\hat{z} \]
is the coordinate of any point inside the photoresist film with its origin at the air–photoresist interface, \( E_1 \) and \( E_2 \) are the amplitudes of the electrical fields of the incident waves that are transmitted through the air–photoresist interface, and \( E_{1r} \) and \( E_{2r} \) are the complex amplitudes of the waves reflected at the film–substrate interface including the phase of the reflection and the losses that are due to the absorption of the incident wave in the film, and \( d = dz \) with \( d \) equal to the film thickness.

The light intensity pattern given by Eq. 1 contains two sinusoidal fringe patterns: one in the \( x \) direction produced by the interference between two incoming waves; and another in the \( z \) direction, which is called a standing wave produced by the interference between each incoming wave and its reflection at the film–substrate interface. The neglected multiple reflections may be represented by a term that multiplies both sinusoidal fringe patterns. This term depends on the film thickness and on the reflectivity of both interfaces. This does not change the relative intensity between the two sinusoidal patterns, but rather the total amplitude, similar to changes in the light intensity. For high reflectivity substrates, the effect of multiple reflections can be neglected completely. For high reflectivity substrates, however, the multiple reflections can strongly reduce the total energy inside the film if the film thickness is not chosen appropriately.

The contrast of the principal interference pattern is better when \( E_1 = E_2 \) and any perturbation on the interference pattern that is due to vibrations or thermal drifts may be represented by a difference between \( E_1 \) and \( E_2 \). Any light scattering or preexposure can be considered by adding a background light intensity \( I_b \) to Eq. 1.

In holographic exposures the photoresist is generally not completely exposed because the requirements of homogeneity and the quality of the wave front generally result in the use of low irradiance in the visible (blue-violet). In such cases the absorption is very poor at 450 nm the absorption coefficient \( \alpha \) of the unexposed positive photoresists is approximately ten times smaller than that for UV light (365–405 nm) and the irradiance is low, requiring long exposure time to saturate the material. In such cases changes in the intensity pattern during exposure because of bleaching (absorption coefficient and refractive-index changes) can be neglected, so that the total exposure energy \( E \) can be found directly by multiplying the irradiance of Eq. 1 by the exposure time \( \Delta t \). For UV exposures for which these approaches are not valid, the exposed energy must be calculated by integration of Eq. 1 during exposure time, taking into account photoresist bleaching.

2.B. Photoresist Response
Although the response of photoresist film to light exposure is frequently described by the function of the photoresist solubility rate \( V \) versus exposure energy \( E \), its overall response also depends on the development process that introduces other nonlinearities. To complete the description of the photoresist response we must also consider the effect of the limit of the spatial frequency response. Therefore we divide this subsection into three parts.

2.B.1. VXE Curve
The VXE curve [photoresist solubility rate \( V \) versus exposure energy \( E \)] represents the response of the photoresist film to uniform light exposures, which depends on the resist–developer system that includes such variables as developer concentration, temperature, and pre bake conditions. This curve can be experimentally measured by using several techniques. Figure 2 shows examples of such curves for Shipley AZ-1350J photoresist films developed by immersion in NaOH solutions for different concentra-

![Fig. 1. Schema of the interfering waves on photoresist film showing the incident and reflected beams.](image-url)
posed photoresist, and were kept at a room temperature of approximately 23°C. The rate along the thickness of the films.

The dissolution rate of the photoresist in a developer solution such as for wet development, the photosensitized resist is dissolved across the whole resist–developer interface. Assuming that this dissolution occurs only at this interface, the mass transport proceeds in the direction normal to it. Neglecting the small effects of induction and adhesion that occur at the first and last skin layer of photoresist (>0.1 µm), the changes in the surface that are due to the dissolution can be described by

$$\frac{\partial \mathbf{r}}{\partial t} = -\mathbf{V} \cdot \mathbf{n},$$

where \( \mathbf{r} \) is the vector that describes each point of the photosensitized surface given by Eq. (5), \( \mathbf{n} \) is the unit vector that is perpendicular to the photosensitized surface:

$$\mathbf{n} = \sin(\varphi) \mathbf{x} + \cos(\varphi) \mathbf{z},$$

\( \varphi \) is the angle between the \( \mathbf{n} \) unit vector and the \( \mathbf{z} \) axis, shown in Fig. 3, and \( \mathbf{V} \cdot \mathbf{n} = V(x, z) \) is the dissolution rate of the photosensitizer in the developer given by Eq. (7) or by the experimental \( V \times E \) curve.

Substituting Eq. (11) into Eq. (10), one can iteratively describe the time evolution of position vector \( \mathbf{r} \) of each surface point as

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) - \mathbf{V}(t) \cdot \Delta t \sin \varphi \mathbf{x} + \cos \varphi \mathbf{z},$$

where \( \varphi \) is calculated from the preceding surface curve at time \( t \) for the same point \( \mathbf{r} \) of the surface.

![Image](https://example.com/image.png)

Fig. 3. Schema of the resist–developer interface with vector \( \mathbf{n} \) perpendicular to the interface at each point \( \mathbf{r} \) and time \( t \).

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The surface profile at each time is represented by an array of \( \mathbf{r} \) vectors.\(^8\) Starting from the array at time \( t \), we apply Eq. (12) to each point of the array and obtain the surface array at time \( t + \Delta t \). Figure 4 illustrates this iterative computing and the evolution of points \( \mathbf{r} \) during the development time. The same figure shows that surface points are created or eliminated as the neighboring points become closer or further away from each other. This procedure can be used to maintain the same precision along the surface and to eliminate unnecessary calculations.

2.B.3. Resolution

The isotropy of wet development introduces stronger nonlinearities than those arising from photosensitization processes. These nonlinearities generate a profile that is rich in tips and that can be represented by high-spatial-frequency harmonics.

When the spatial frequency becomes higher, the photoresist does not record as well, as thin tips do not appear in the experimental profiles. This phenomenon, generally called loss in resolution, occurs because of several effects such as chemical diffusion of photoactive\(^9\) and developer species, dependence of the development rate on surface curvature,\(^15\) mean distance between photosensitive molecules,\(^16\) and the size of the smallest particle of photoresist that is removed by the developer. The modeling of each effect separately complicates the simulation because it is not always possible to distinguish the effect that limits the resolution and constitutes a problem for most of the profile simulations.\(^9,17\) In this way an interesting approach is to describe the loss of the resolution of the complete process as a high-spatial-frequency filter.

Although the complete process of the photoresist does not behave like a linear system, its limited frequency response can be assumed to be a linear space-invariant filter (LSIF).\(^18,19\) A LSIF can be completely described by its modulation transfer function (MTF), which represents the filter response for each spatial sinusoidal signal. Although each step of the process has its intrinsic resolution limit, we can define a MTF for the complete process (including development).

The complete response of the photoresist can then be treated as a cascade of a nonlinear response of the photoresist and the LSIF. So if we calculate the profile in the photoresist that results from the exposure and development processes, the final profile can be obtained by applying a MTF to each spatial harmonic of the profile and then synthesizing the final profile again.

Assuming a simplified MTF as illustrated in Fig. 5, this procedure can be numerically performed. This MTF corresponds to a linear cut in the response, starting at the period \( \Lambda_2 \) and finishing at \( \Lambda_1 \). \( \Lambda_2 \) corresponds to the smallest dimension that can be recorded without cut off, and \( \Lambda_1 \) is the smallest dimension that can be recorded at all.

Figure 6 illustrates the effects of this filter application on the profile of a grating.

3. Results and Discussion

The simulation described above was performed by using a simple IBM PC-compatible microcomputer and was used to compute the profile of gratings recorded holographically in films of Shipley AZ-1400 photoresist on glass and Si substrates under wet immersion development. The initial film thicknesses were assumed to be much larger than the period of the gratings so that the substrate was not reached.

For filtering purposes the simple MTF function proposed above was employed. The initial and final cutoff periods were determined by comparing the simulated profiles with those obtained by scanning electron microscope (SEM) photos of the cross section of gratings with periods of 0.8 and 1.6 \( \mu \)m, recorded in AZ-1400 photoresist films on glass and Si substrates, respectively, in linear conditions. The shapes were compared taking into account the definitions of standing waves for glass substrates and edges for Si substrates. This comparison leads to cutoff periods of \( \Lambda_2 = 0.6 \mu \)m and \( \Lambda_1 = 0.1 \mu \)m. These periods provide information about the smallest structure dimension that can be recorded by this technique. This limit depends only on the intrinsic limit of the photoresist and the wet development process and not on the exposure pattern or stability of the holographic setup.\(^20\)

Figure 7 shows the evolution with development time for the computed cross section of relief holographic gratings. These were recorded on glass substrates using the same exposure energy and two different development conditions: (a) for a nonlinear \( V \times E \) curve corresponding to low concentration of the developer and high-exposure energy, (b) for a linear \( V \times E \) curve (corresponding to high concentration of developer or small exposure energies), and (c)
the same as with a light background. The refractive index and the absorption coefficient used in the computations were, respectively, \( n = 1.67 \) and \( \alpha = 0.08 \, \mu m^{-1} \) at \( \lambda = 0.4579 \, \mu m \) for Shipley AZ-1400 photoresist. For the glass substrate a value of \( n = 1.51 \) was assumed. For such values there are no observable effects from the light decay through the film because of absorption and from the standing waves because of reflection at the photoresist–glass interface.

As described by Austin and Stone,\(^2\) the development in strong nonlinear conditions\(^3\) Fig. 7a produces a squarelike profile even for sinusoidal pattern exposures. On the other hand, the isotropy of wet development produces a narrowing of the top of the structures.\(^2^1\) This effect is particularly pronounced for linear development conditions and long development times (deep gratings). In these cases a strong shift from the expected sinusoidal profiles is observed [Fig. 7b]. Figure 8 shows SEM photographs of the cross section of a deep photoresist grating recorded in AZ-1400 photoresist film on glass substrates. The exposures were performed in a self-stabilized holographic setup\(^2^2\) at \( \lambda = 0.4579 \, \mu m \). The total exposure energies were 150 mJ/cm\(^2\) [Fig. 8a] and 200 mJ/cm\(^2\) [Fig. 8b], respectively, and both gratings were developed in AZ-351 developer diluted 1:3 in deionized water for 1 min. These conditions correspond approximately to a linear \( V \times E \) curve. Note the strong narrowing of the peaks as described by the model.

Figure 7c shows the same recording in linear conditions as that shown in Fig. 7b but with background light. Note that, because of the effects of isotropy, the maximum aspect ratio (depth/period) of the resulting grating depends strongly on background light and not only on isotropy itself as proposed by Zaidi and Brueck.\(^2^3\) This fact indicates that the use of high-stability holographic setups is indispensable in order to realize high aspect ratio gratings. Some grating profiles that are recorded in nonstable conditions, as, for example, holographic recording inside...
liquids, exhibit the characteristic shape shown in Fig. 7c. Note also that the nonlinearity of the $VXE$ curve produces effects that are opposite isotropic ones (an enlargement of the top of the structures). Thus the nonlinear conditions of the $VXE$ curve should be used to produce high aspect ratio gratings and to preserve the sinusoidal form in deep gratings, particularly in the presence of background light.

Figure 9 shows the same evolution curves as those in Fig. 7 but for Si substrates ($n = 4.58, \alpha = 3.57 \mu m^{-1}$) developed in nonlinear and linear conditions. Those developed in linear conditions were done with and without background light. Note that, as described in the literature, the standing waves produce energy nodes so strong that the gratings rapidly assume a squarelike profile that develops as a sidewall structure (Fig. 9c). Figure 10 shows a SEM photograph of the cross section of a photoresist grating. This was recorded in AZ-1400 photoresist film on Si substrates using the same experimental conditions as were used for Fig. 8 illustrating this squarelike profile.

The nonlinear development conditions amplify the enlargement of the peaks caused by standing waves, producing a lateral etch under the nodes of the standing waves. Such an effect can be useful for preparing shadow masks for lift-off processes. This effect is less pronounced in linear conditions because it favors the narrowing of the top of the structures.

The presence of background light attenuates the effect of the standing waves, particularly in linear conditions for which the effect of the narrowing of peaks caused by isotropy is larger.

4. Conclusions

In spite of its simplicity, the simulation that we have developed here is a good description of the recorded profile on photoresists under holographic exposures. Our simulation takes into consideration only the more effective process effects in the profile, such as photosensitization response of the photoresist, standing waves, isotropy of wet development, and the cutoff of high-spatial-frequency harmonics. Other effects, such as changes in the dissolution ratio, multiple reflections, the ending of film, or different light patterns, that have not been treated in this simulation can be easily introduced.

The simulation can be used to study the influence of experimental conditions on the shape of the profile and can be used to optimize holographic recordings. To exemplify the potential of our device it was used to compute the resulting profile of AZ-1400 photoresist films on glass and Si substrates. The strong influence of isotropy of wet development on the shape of photoresist gratings on glass substrates has been shown. We amplified this effect by using linear development conditions and background light, but we attenuated the effect by using nonlinear development conditions. For exposures on high-reflectivity substrates such as Si wafers, the standing waves strongly influence the shape of the relief profiles. If the initial film thickness is conveniently chosen, this effect can be used to produce squarelike profiles that are more resistant for use as a mask for etching or as shadow masks for lift-off processes. If the experimental conditions are well known, in particular the $VXE$ curve, the simulation can be used to fit the experimental profiles.

An additional use of the model is the evaluation of the resolution limit of photoresist processing. The

![Fig. 9. Evolution of computed profile gratings of 1.6-µm period exposed at $\lambda = 0.4579 \mu m$ in photoresist films over Si substrates for three different conditions: (a) strong nonlinear $VXE$ condition, (b) linear $VXE$ curve, (c) linear $VXE$ curve with a light background.](image)

![Fig. 10. SEM photograph of the cross section of a holographic grating of 1.6-µm period recorded on a Si substrate.](image)
resolution limit produces an attenuation effect of the interference pattern that is similar to background light and causes the collapse of the peaks. In terms of sinusoidal harmonics this effect can be explained as a decay of the amplitude of the higher-spatial-frequency harmonics. Such a limit is difficult to obtain from direct measurements because of mechanical vibrations on holographic setups. The standing waves, however, are high-spatial-frequency light signals that are quite insensitive to vibrations. Thus the fitting of the profile of standing waves can be used as a method to evaluate the resolution limit of photosensitive materials and processes, as has been illustrated in this paper.

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References and Notes


