Photoresist characterization and linearization procedure for the gray-scale fabrication of diffractive optical elements

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We present a procedure for the characterization and the linearization of the photoresist response to UV exposure for application to the gray-scale fabrication of diffractive optical elements. A simple and reliable model is presented as part of the characterization procedure. Application to the fabrication of surface-relief diffractive optical elements is presented, and theoretical predictions are shown to agree well with experiments. © 2001 Optical Society of America

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1. Introduction

Diffractive optical elements (DOEs) are passive devices that redirect and focus light through the mutual interference of propagating waves. In general, a DOE consists of a surface-relief profile etched into an optically transparent substrate such that the phase profile imparted to the incident field results in a specific diffraction pattern. Although several methods exist for the fabrication of such profiles, by far the most commonly used method is that of the microphotolithographic process. In this case a binary chrome-on-glass photomask is used to pattern photoresist profiles that represent the desired DOE profile in much the same way as in the fabrication of integrated circuits.

To create a multilevel DOE with standard binary masking techniques, one must use multiple masks as well as multiple alignments and exposures.[1] As such, this approach requires N masks—and therefore N processing steps—to achieve 2^N levels. However, three-dimensional structures of this type that contain features of the order of or smaller than a micrometer are difficult to fabricate by use of this process.[2,3] Consequently, an alternative process based on gray-scale photomasks has recently been developed that, in contrast to the binary process, allows the fabrication of an N-level profile by use of only a single mask and therefore a single processing step.[2,3]

Because the gray-scale photolithographic process is more time efficient and less prone to alignment errors, it is becoming increasingly popular for the fabrication of multilevel DOEs. However, critical factors in the development of a gray-scale process is the characterization and the linearization of the photoresist response to UV irradiation. Although most photoresists are engineered to be highly nonlinear (as is required in the fabrication of microelectronic circuits), one can obtain a linear response by adjusting the exposure and the development processes. Because there are many processing parameters that affect the photoresist response, developing and refining a recipe for gray-scale photolithography can be quite challenging. Therefore, in this study, we developed a simple and reliable model based on processing parameters that accurately predicts the response characteristics of the photoresist to UV exposure. To the best of our knowledge, such a process developed explicitly for the fabrication of DOEs has not been presented previously. Therefore, in the remainder of this paper, we present our model and discuss experimental results that illustrate its utility.

2. Multilevel Fabrication

The initial step in the gray-scale fabrication of DOEs is to design the phase profile that is to be realized in the DOE. This is typically done by use of design algorithms based on scalar diffraction theory.[1,4–6]

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However, for DOEs that have individual feature sizes that approach the wavelength of illumination vector methods become necessary.[7,8] After the three-dimensional profile is designed it is encoded into a suitable file format, e.g., GDSII or Caltech Intermediate Format, and written onto a gray-scale mask. This last can be done with direct-write *e*-beam lithography to create a gray-scale mask on high-energy beam-sensitive glass[9,10] or with high-resolution printing methods to create gray-scale photographic plates.[11–13]

After the mask is in hand the gray-scale fabrication procedure for a multilevel DOE is as follows:

(1) Spin-coat a smooth substrate with a thin film of photoresist.
(2) Place the sample in intimate contact with the mask and illuminate it with UV light to expose the resist film.
(3) Develop the resist to obtain a multilevel surface profile.
(4) Transfer the pattern from the resist layer into the substrate.

In general, pattern transfer is achieved by the etching of the surface of the substrate by use of either wet- or dry-etching techniques.[14–16] For this discussion, we treat photolithography and etching as two independent processes and focus on the former. Therefore, in the remainder of this paper, we concentrate on producing high-fidelity three-dimensional profiles in photoresist through contact photolithography by using a gray-scale mask.

In gray-scale lithography the photoresist profile is controlled primarily by the local transmittance T_n or the optical density OD_n of the gray-scale mask. The subscript n is used to denote a discrete gray-scale level in the mask. Unlike the binary method gray-scale photolithography depends on a partially developed photoresist; consequently, control over the exact development depths is critical to one's being able to realize the desired profile. As a result, one must precisely designate the transmittance levels of the gray-scale mask in accord with the desired surface-relief structure. However, to determine the requisite transmittance level, one must first characterize the chemical response of the photoresist to the UV exposure. Although this requirement is also true in standard microlithography, it is somewhat more straightforward in the case of gray-scale lithography because of the requirement of having to resolve only two levels. In this application the engineered nonlinear response of the photoresist, which is deliberately emphasized in microelectronics to improve resolution, is working with you. In the case of gray-scale lithography this nonlinearity presents a significant obstacle because intermediate exposure levels are absolutely necessary. Consequently, in this paper, we present a characterization procedure that is explicitly targeted at the linearization of the photoresist response to UV irradiation for DOE fabrication.

In the course of this study, we first investigated the various properties of both negative and positive photoresists. Because positive resists are more amenable to a linear process, they were used in this study. Thus we begin with a brief overview of the properties of positive photoresist.

A positive photoresist comprises three basic constituents: a base resin, a photoactive inhibitor, and a solvent. The concentration of inhibitor strongly influences the dissolution rate of the photoresist in a developer solution. Thus during exposure with UV radiation the inhibitors are destroyed, thereby locally altering the dissolution rate of the photoresist film. Theoretical models based on material parameters for different photoresists describe the precise nature of inhibitor destruction with UV radiation.[17–21] Experimental schemes have also been devised to measure these parameters directly.[22–26] Typically, the concentration of inhibitor fluctuates throughout the thickness of the resist layer as well as laterally across the surface of the film. In addition, the optical absorption tends to vary over the time span of exposure. Thus the exposure and the absorption processes on the molecular level are difficult to characterize and model. Moreover, the development of a photoresist also depends strongly on the resist chemistry, the developer chemistry, and previous processing, e.g., bake out. As a result of all these factors, the dissolution rate of exposed photoresist tends to exhibit a strong nonlinear behavior with respect to inhibitor concentration.

Although we did not fully characterize the exposure and the development processes on the molecular level, we combined the various properties into a macroscopic analysis in an attempt to reach a simple and practical result, namely, the functional relation between the dissolution rate and the mask transmission. Such a characterization is commonly called a Hurter–Driffield curve, or a contrast curve, for photoresist and is discussed thoroughly in the literature.[27] Our goal in this paper is the characterization of the response of the photoresist in a gray-scale lithography process to identify the optimal distribution of OD values for a gray-scale mask, as is required in the fabrication of DOEs. The theoretical model presented in Section 3 focuses neither on polymer chemistry nor on optical absorption by photoinhibitors. Similarly, we do not describe the physical or the chemical interactions on the molecular level; rather, we present a simple and reliable model to capture the main properties of the gray-scale lithographic process that are needed to realize high-fidelity multilevel DOEs. The process that we developed during this study is presented next.

3. Model for Photoresist Linearization

To develop our model of photoresist response, we assumed that the initial photoresist layer consists of material C and that, on exposure to UV irradiation, it is chemically changed into a second material, which we call material S. We know that the transformation from material C to material S occurs over a period of time; however, we assumed that there were

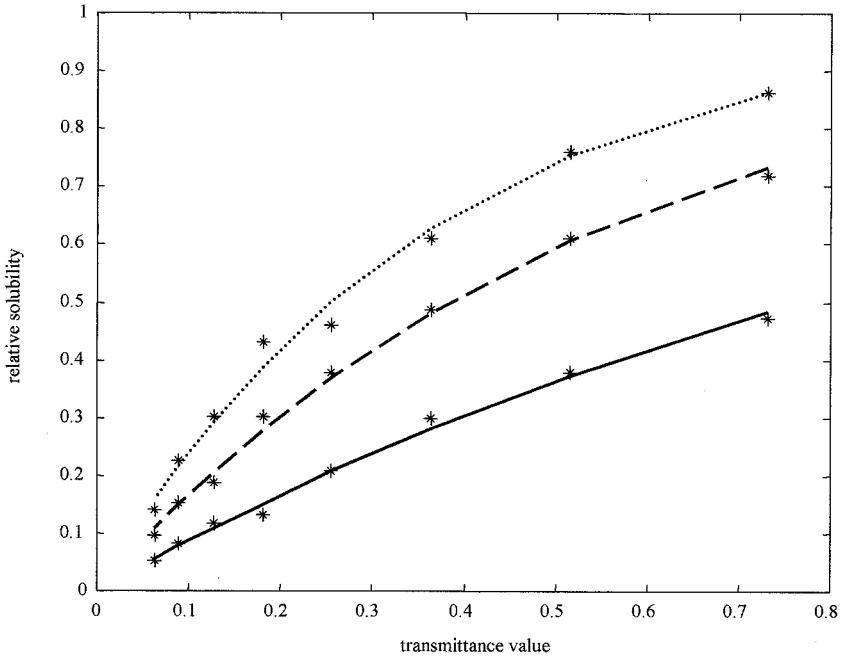

Fig. 1. Solubility plotted versus the transmittance for the photoresist samples. Solubility was inferred from the profile depth after development, and values are normalized with respect to the percentage of remaining photoresist. The asterisks represent experimental measurements; the solid curve represents our model for an 8-s exposure time and $\kappa = 0.9053$; the dashed curve fits the model for a 16-s exposure time and $\kappa = 1.8106$; the dotted curve corresponds to a 24-s exposure and $\kappa = 2.7159$ [Eq. (7)].

no intermediate materials for the sake of simplicity. When placed in the developer material C and material S have different solubilities, which can be observed from their different development rates. For a positive photoresist, the development rate of material C is denoted D_C, and the developing rate of material S, D_S. For a negative photoresist, $D_C \gg D_S$. In the gray-scale process, unlike the binary technique, the transformation from C to S over the extent of a given feature is not complete. The resultant photoresist film is then locally composed of both material C and material S. In the following derivation, we denote the *percentage* of material C as C and the *percentage* of material S as S.

Now consider a positive photoresist for which initially at $t = 0$ the film is entirely unexposed:

$$S_{t=0} = S(0) = 0,$$
$$C_{t=0} = C(0) = 1. \tag{1}$$

The film is then transformed during an exposure interval Δt. We assume that the change ΔS is proportional to the amount of unchanged material C and to the intensity I of UV light, according to

$$\Delta S(t) = \mu C(t) I \Delta t. \tag{2}$$

The constant μ is the optical response parameter, which describes the material's sensitivity to UV irradiation. Because the total amount of photoresist is conserved in the process, we have

$$C(t) + S(t) = 1. \tag{3}$$

Thus solving Eqs. (2) and (3) and enforcing the initial condition in Eqs. (1), we have

$$S(t) = 1 - \exp(-\mu I t). \tag{4}$$

In the gray-scale technique the intensity is spatially controlled by the mask, which has a transmittance T. The intensity of light that reaches the photoresist is $I = I_0 T$, where I_0 is the intensity without the mask. Thus after t_0 seconds of exposure the final percentage of material S is

$$S = 1 - \exp(-\mu I_0 T t_0). \tag{5}$$

The depth of the developed photoresist is proportional to the solubility of the final material, which is also proportional to S:

$$\text{solubility} = D_S S + D_C(1 - S) = D_C + (D_S - D_C)S. \tag{6}$$

If we define a new variable $\kappa = \mu I_0 t_0$, Eq. (4) becomes

$$S = 1 - \exp(-\kappa T). \tag{7}$$

Interestingly, from Eq. (5) the percentage of chemical change in the resist is not directly linear to either the transmittance or the OD. To see this relation more clearly, consider Figs. 1 and 2, which illustrate the different behaviors of the positive photoresist as κ is varied. For a small value of κ the depth in the photoresist is almost directly proportional to the transmittance, whereas for large values of κ the depth is more linear with respect to the OD. Note now that κ not only depends on μ, which we assume

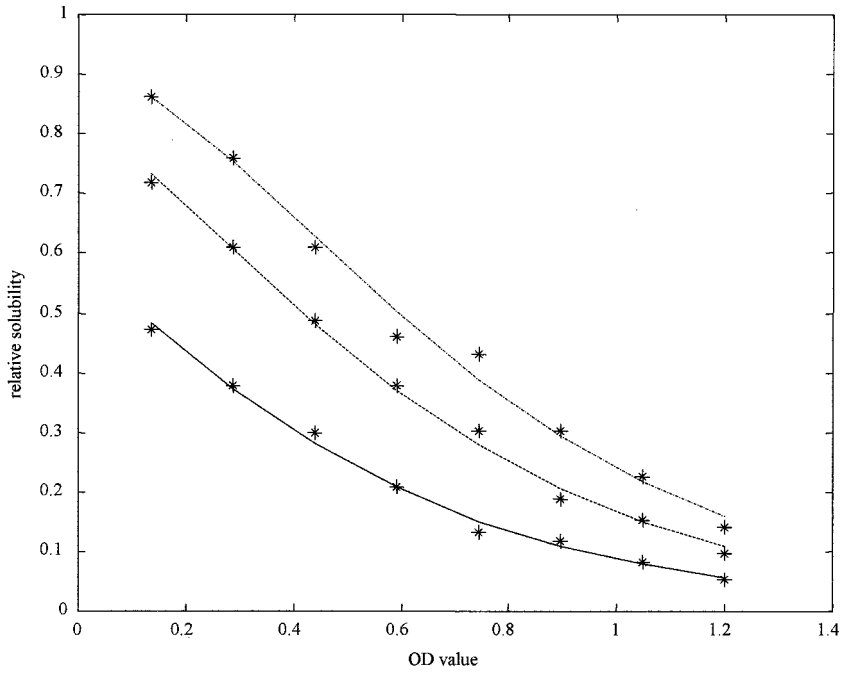

Fig. 2. Solubility plotted versus the OD for the photoresist samples. All definitions, parameters, and representations are as for Fig. 1.

is a constant material property, but also depends on the exposure energy, $E_0 = I_0 t_0$. Thus, by modifying the exposure energy (typically by varying the exposure time), one can render the photoresist response quasilinear with respect to either T or OD. We found experimentally that higher exposure energies—and therefore higher values of κ—yield the most reliable results. Hence we designed our gray-

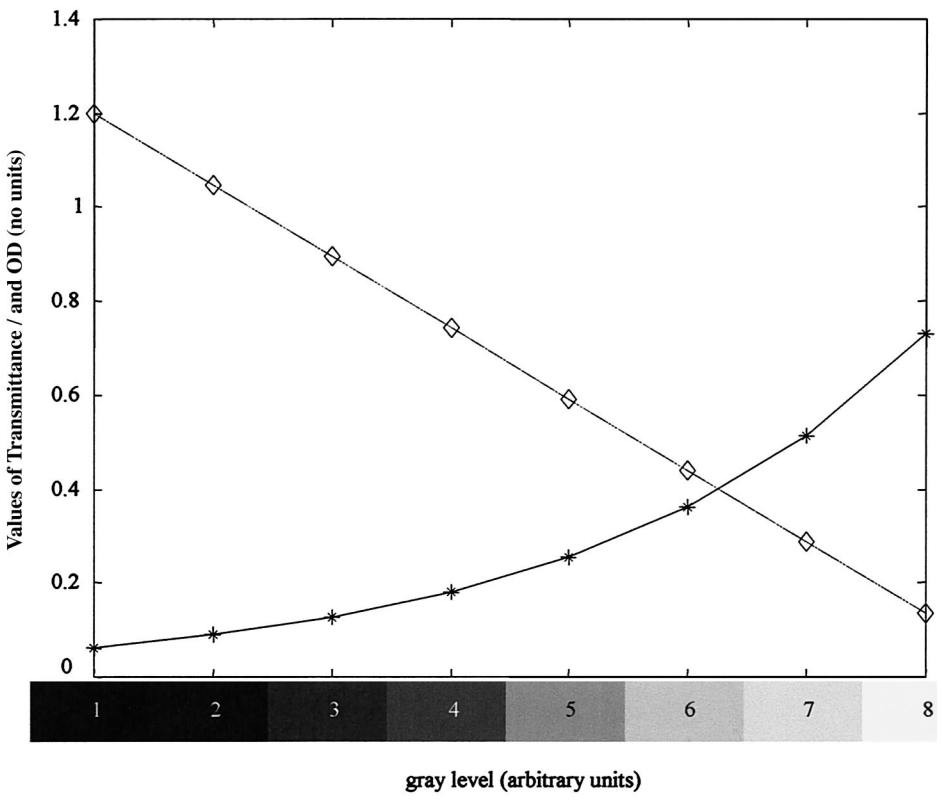

Fig. 3. Values of the discrete transmittance (asterisks) and the OD (diamonds) plotted for the gray-scale mask. The mask has eight gray levels distributed linearly across a wide range of ODs.

Table 1. Photoresist Fabrication-Process Recipes Used to Obtain the Experimental Results Shown in Fig. 4[a]

	Soft Bake		Hard Bake			
Photoresist AZ5214E	Time (s)	Temperature (°C)	Time (min)	Temperature (°C)	Exposure (s)	Develop Time (s)
Sample 1	30	90	5	120	8	14
Sample 2	31	90	5	120	16	7
Sample 3	32	90	5	120	24	5.5

[a]For all exposures the UV energy level was 18 mW/cm^2. The developer was 327 MIF.

scale mask to have evenly spaced levels with respect to the OD. Note that even the solubility-to-OD relation is not exactly linear. If we want to achieve a perfect mapping of the OD to the developed depth, we have to find the value of μ that is associated with the photoresist. Although we realize that no material can be fully characterized by a single parameter, we demonstrate the utility of our simple model in Section 4.

4. Experimental Results for Photolithography and Profilometry

For calibration of the photolithographic process, we used a test mask that included eight adjacent rectangles of a 10-μm width. The gray levels of the rectangles were spaced evenly with respect to the OD on the basis of the aforementioned model. Figure 3 shows the transmittance and the OD values for the gray-scale mask.

All samples were made with Clariant AZ5214E photoresist on glass substrates. The samples were spun at 7000 rpm for 40 s to achieve a resist thickness of approximately 1 μm and baked for 30 s at 90 °C. The exposure intensity was held at 18 mW/cm^2. Table 1 shows the recipes for preparation of the three photoresist samples that were used to characterize our model.

After fabrication, we used a WYKO Model RST 500 profilometer to measure the surface characteristics of the multilevel DOEs. Because the operation of the profilometer is based on reflection white-light interferometry, the optical properties of the materials being measured must be considered. For example, photoresist on silicon is difficult to profile because of

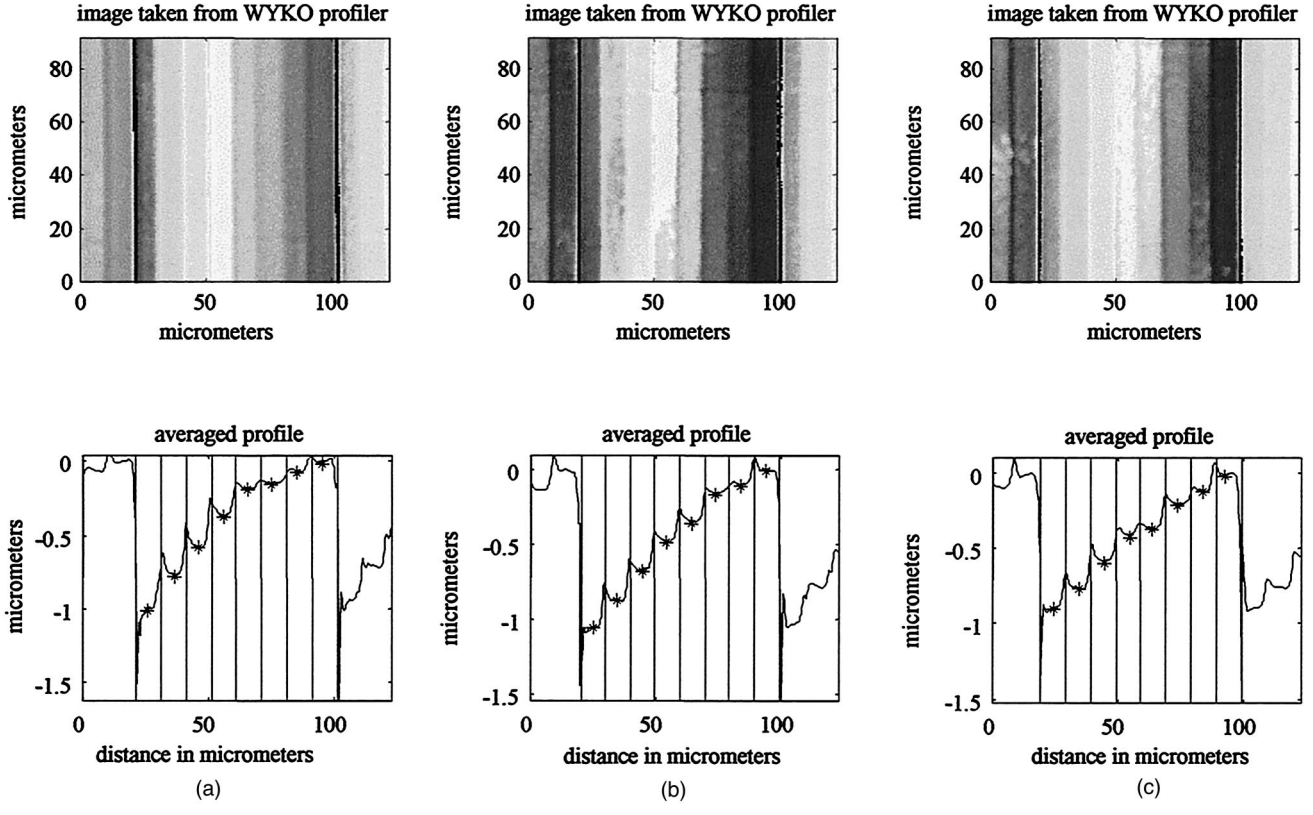

Fig. 4. Test-pattern profiles for the three photoresist samples. The vertical lines in the graphs of the average profiles represent step boundaries; the asterisks mark the average height of a step. Samples were exposed and developed, respectively, for (a) 8 s and 14 s, (b) 16 s and 7 s, (c) 24 s and 5.5 s.

the drastic difference in the reflectivities of the materials. Photoresist and glass, however, have similar optical properties, so interferometric measurements are very useful. Typically, we used glass substrates during the photolithography calibration process for this reason. Also, features with large slope angles (>20°–30°) may induce some measurement error (because of the low reflectance of steep profiles), so we concentrated on relatively shallow structures. We then measured the test patterns after exposure and development.

Figure 4 shows the photoresist height plotted versus the transmittance for three samples. As the exposure time increases, we can see the behavior transform from linear to the transmittance to linear to the OD. If we set $\kappa = 0.90$ for an exposure time of $t_0 = 8$ s all the theoretical analyses agree well with the experimental results for different exposure times.

5. Discussion and Analysis

From our analytical and experimental investigation of gray-scale photolithography, we found that the exposure energy plays an important role in the response behavior of photoresist. Of course, other parameters like the soft-bake temperature and time also have significant effects, but in a repeatable process they should be held as constant as possible and can therefore be lumped into the parameter κ. In this study, we show only the results obtained from a process that used a 30-s soft bake at 90 °C because this approach offered us the best resist profiles. In comparing the experimental results with our theoretical model, we found good agreement.

We tested the effect of exposure energy by using three different exposure times: 8, 16, and 24 s. The shape of the resist profile changed accordingly. Because κ is proportional to t_0, we know that $\kappa_{24} = (3/2)\kappa_{16} = 3\kappa_8$. We did a search to κ_8 by finding a best fit for these three profile data simultaneously. For our recipe, we found that $\kappa_8 = 0.905$ for 8 s. Using $\kappa = \mu I_0 t_0$, with $I_0 = 18\ \mathrm{mW/cm^2}$, we found that $\mu = 6.9 \times 10^{-3}\ \mathrm{cm^2/(mW\ s)}$. This is the optical response parameter for Clariant AZ5214E photoresist, according to our process.

6. Conclusion

In this paper, we have presented a simple and reliable procedure for the fabrication of multilevel DOEs by using a gray-scale photolithographic process. We have also presented a theoretical model of the photoresist response and introduced an optical response parameter that describes the chemical sensitivity of photoresist to UV exposure. With our model and experimental results, we were able to determine the optical response parameter of photoresist AZ5214E. Having characterized the response of the photoresist, we were able to design a gray-scale mask with eight discrete levels that were linearly distributed in OD. We were able to refine an exposure and development procedure that reliably produces multilevel DOEs in photoresist.

Our method of gray-scale lithography yields high-efficiency DOEs without tedious iteration or the susceptibility to error that is associated with multiple-registration and multiple-exposure methods. Our theoretical model, although extremely simplified, is quite useful and can be adjusted to handle multiple materials and negative photoresists. The optical response parameter that we have introduced in this paper is intended only for the process presented in this paper. Different processes, i.e., different soft-bake temperatures and times, will change the behavior of the photoresist and can be described by a change of the optical response parameter.

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