Response curve for photosensitive films: a derivative method

Lucila Cescato, Geraldo F. Mendes, and Jaime Frejlich

A derivative technique is developed for measuring the material response of photosensitive films. The method consists of recording a low modulated grating superimposed with different uniform preexposures. The modulation of the resulting shallow gratings recorded on the photosensitive film is measured by diffraction techniques and the derivative response is thus computed. Compared with other diffraction-based methods, this one is not affected by nonlinearities. Qualitative visual monitoring of these diffraction data may be used for optimizing materials and processes in photolithography and optical recording. Some experimental results concerning positive and negative photoresists are presented.

I. Introduction

The response curve[1] of a photosensitive film is of the highest importance in most applications. The lack of linearity in photosensitive film response is a serious handicap in image and holographic recording,[1,2] and it strongly limits the possibilities of spatial multiplexing techniques.[3] On the other hand, high resolution photolithography takes advantage of the nonlinearity of photoresists in producing binary recording for masking purposes. It may also be useful for recording dense features in optical data storage systems.[4] In any case, knowledge of the response curve of a photosensitive film allows the best conditions for exposure to be chosen in order to reduce noise and improve resolution.[5] The response curve of most photosensitive materials may sometimes be significantly modified[6] during wet processing to fit the user's objectives.

The way the linearity is defined depends on the specific use intended for the film. For holographic recording it is convenient to define it in terms of the diffraction efficiency as described by Lin.[2] For characterization of the material itself, however, or for optical components fabrication and photolithography it is advantageous to describe it in terms of its material response.[1]

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This paper describes a new method for experimentally determining the material response of a photosensitive film in terms of its exposure energy derivative. It will be shown that this method has some advantages over the currently employed ones.

II. Material Response

The material response of a photosensitive film may be defined by the relation

$$\beta = g(E), \tag{1}$$

where β represents whatever optical parameter (refractive index, optical thickness, absorption coefficient, etc.) may be modified by the action of light and subsequent development, and variable E represents the exposure energy. For most photoresist films where light is recorded as a surface modulation, β may be represented by the film thickness h remaining after exposure and development. The response curve ($\beta = h$ vs E) may be straightforwardly measured by exposing a film with different uniform values of E and measuring the corresponding h. This should be considered a direct or continuous method as it is only concerned with low (or zero) spatial frequency input signals (uniform exposure patterns). As with all such methods it is difficult to measure h with precision and to avoid the effect of spatial noise either from the exposure light or from cosmetic film defects. Bartolini[6] measured the response of a positive AZ-1350 photoresist from Shipley in this way. He aluminized the film after exposure and development to use Tolansky's interferometric techniques and to increase precision of measurement.

An indirect way of measuring the response curve consists of recording a diffraction grating on the film using different average exposure energies E. The first-order diffraction efficiency for such a grating is

measured, from which data its geometrical modulation h (peak-to-trough) is computed. In fact, the efficiency of first-order diffraction for a sinusoidal thin phase grating in air is[5,7]

$$\eta = J_1^2(\phi/2) \text{ with } \phi \equiv 2\pi(n-1)h/\lambda, \qquad (2)$$

where J_1 is the first-order Bessel function, n is the film refractive index, and λ is the test wavelength. Jenney[8] employed this method with a photopolymer film using a sinusoidal 110-lines/mm unit contrast exposure pattern. This method largely facilitates measurements compared with the continuous one above, because diffraction efficiencies may be measured with good precision and are less sensitive to spatial noise. This is why gratings have been used extensively for characterization and testing of photosensitive films. This method however has some limitations:

(a) The sinusoidal shape of the recorded grating cannot be assured for increasing values of its modulation because of the lack of linearity of material response of most films. In that case Eq. (2) will not apply throughout the whole range of measurements.

(b) Increasing values of E are generally associated with increasing exposure times which will result in increasing background and other noises. Disturbances, such as long-term thermal drift, which are not directly proportional to exposure times are the most difficult to handle. This will obviously interfere with the measurements.

(c) The recording of rather large grating modulations limits the applications of this method to rather low spatial frequency patterns if we want to keep within the Fraunhofer diffraction theory limits ($h <$ grating period) so that Eq. (2) is verified.

III. Derivative Technique for Material Response Measurement

We have recently shown[9,10] that the modulation of a shallow grating may be accurately computed from its diffraction spectra. Lamellar grating modulations as low as 20–30 Å were so measured.

In this paper we are using this technique to develop a differential (or derivative) method for measuring the material response of a photoresist film. This method is free from the handicaps reported in Sec. II. The film is exposed using a constant low modulated pattern of amplitude ΔE superimposed with a uniform exposure energy E. Figure 1 describes the exposure pattern and the resulting profile modulation recorded on a typical negative photoresist after development. A low modulated lamellar phase grating is so recorded on the film. A low-power He–Ne laser beam is directed nearly normal to the grating surface; its diffraction spectra are measured and data processed as in Ref. 10 for a shallow transmitting lamellar grating. Using an adequate nomogram[10] or simple computation, the corresponding grating peak-to-trough modulation Δh is obtained. The sample was then aluminized and the same process carried out for measuring Δh for reflecting diffraction. Both data should agree. Experimental data representing the derivative response curve of the film measured by transmission diffraction are then plotted as $\Delta h/\Delta E$ vs E. Figures 2 and 3 show such data obtained for positive and negative commercial photoresists.

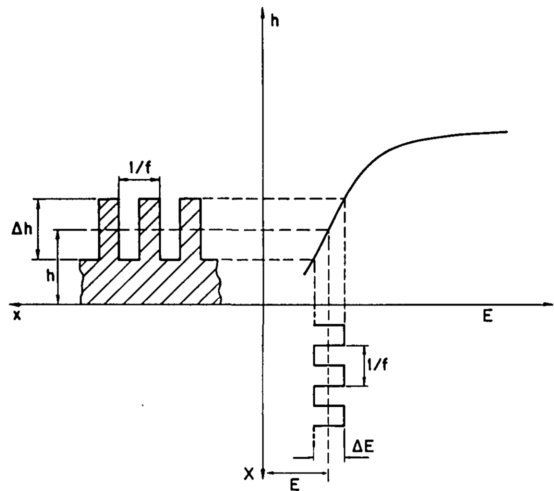


Fig. 1. Derivative technique schema. A low-modulated (ΔE) lamellar pattern of light of period $1/f$ and average energy E is projected on a photoresist thin film having a material response curve (h vs E) as represented. After exposure and developing a lamellar grating results of period $1/f$, thickness modulation Δh, and average thickness h. The quantity $\Delta h/\Delta E$ represents the response curve derivative.

A. Experimental Results

This method was employed for measuring the response curve of a Kodak negative resist (KMR-747, 60 cs) and a Shipley positive resist (AZ-1350B). Both photoresists were coated on a glass substrate (62 × 62 × 1.5 mm) using a spinner (from Headway Research, Inc.). Films were prebaked for 20 min at 90°C. KMR-747 films were developed for 60 sec with Kodak developer 1918630 and rinsed for 15 sec with Kodak rinse 1919786. AZ-1350B films were developed for 60 sec using a homemade concentrated developer (NaOH 1.06 N in deionized water) and developing was stopped with deionized water. In all cases films were dried with a pure nitrogen gas jet. Exposures were performed using a model 686B photoaligner from Photolithographic Products using a high-pressure Hg vapor lamp providing a collimated light beam of 6.7 mW/cm^2. The test gratings were recorded by contact-printing photolithography using a lamellar grating amplitude mask of 100-μm period and 50-μm bar size prepared on a Kodak high-resolution emulsion plate type 1A. Figure 2 shows the derivative curve and computed integral curve for positive AZ-1350B photoresist films of different thicknesses and developed in different conditions.

All results were compared with the measured intial film thickness h_0. The latter was measured by recording a step on the film down to the substrate, aluminizing it, and measuring it using interferential microscopy techniques.[11] The maximum values for the integral curves agree with these h_0 data within the latter's uncertainty limits (±150 Å) as seen in Fig. 2.

Figure 3 shows the derivative curve measured for negative KMR-747 film. The integral response curves were independently measured by recording full modu-

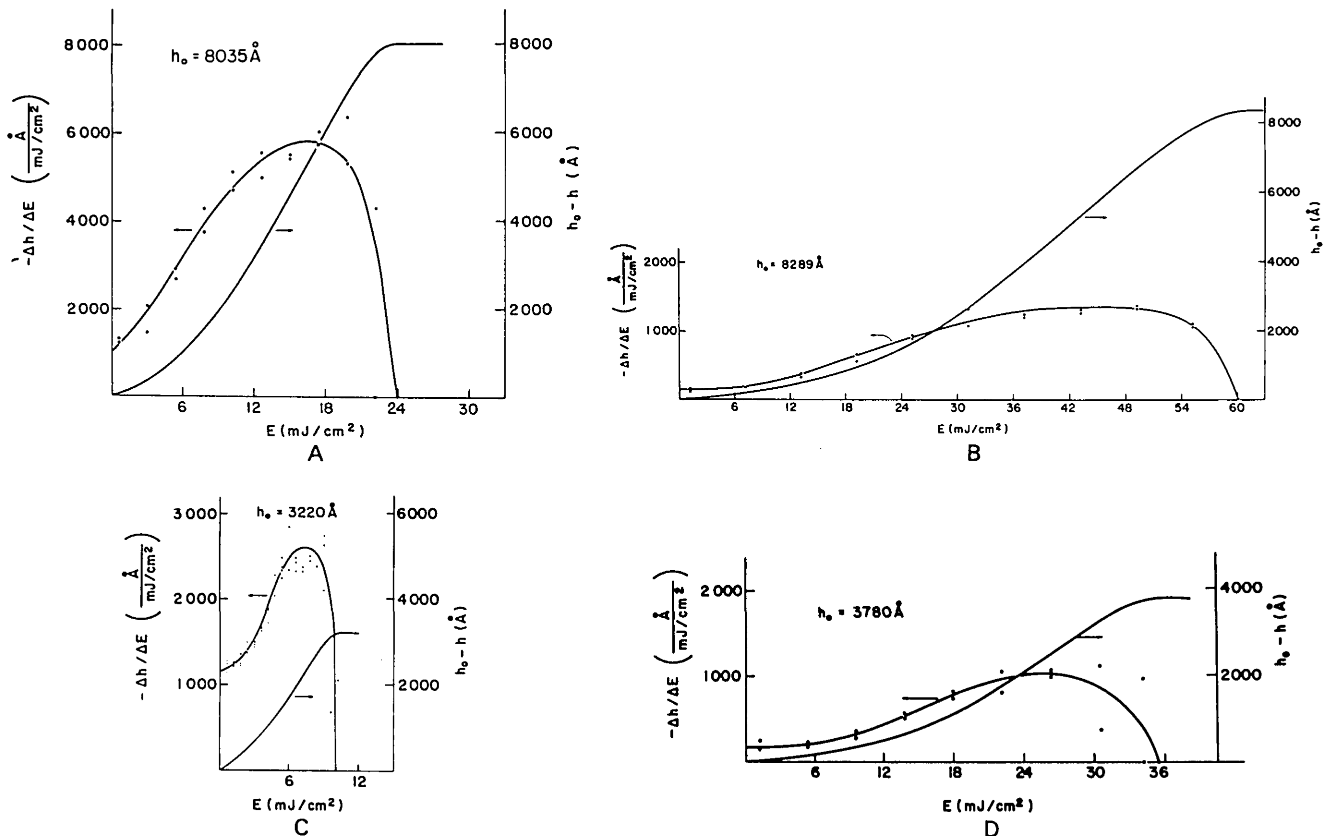


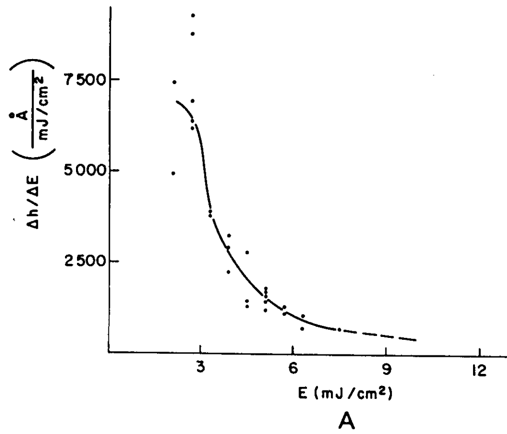
Fig. 2. Derivative response curves for AZ-1350B photoresist. Experimentally measured derivatives and their computed integral curves are shown for a film coated using a spinner at 1000 rpm and developed with NaOH 1.06-N water solution diluted (A) 1:8 and (B) 1:14. The same curves are shown for another film coated at 4000 rpm and developed with the same NaOH solution diluted (C) 1:8 and (D) 1:14. The derivative and etched thicknesses are represented on the ordinate on the left- and right-hand sides, respectively; h represents the remaining film thickness. The reported initial film thickness h_0 was measured by interferential microscopy as described in the text, with an estimated ±150-Å uncertainty.

lated lamellar gratings and computing its modulation from diffraction spectra as described for the indirect method[8] in Sec. II. Some particular features of this photoresist do not allow computing the curve from the experimentally measured derivative, as was done for the positive resist. Note that the KMR-747 has a threshold energy of $\sim$2.7 mJ/cm^2. That means that up to that limit, not enough cross-linking is developed in the film to assure a uniform film on the substrate. The derivative of the negative resist response curve is larger at the beginning where the threshold limit does not allow any measurements to be carried out. The larger derivative values which are most relevant for integration are ill-defined or not defined at all, so that integration is rather indeterminate and not worth performing.

For comparison, all response curves in Figs. 2 and 3 were normalized to h_0 and plotted in Fig. 4. Note that the negative resist is steeper at the beginning (more sensitive than a positive resist) and shows an energy threshold which does not appear with positive resists. Note also that normalized negative resist curves are similar for different h_0 which is not the case for positive resist curves. Note also the striking influence of developer concentration in positive response curves.

B. Qualitative Monitoring

This method allows useful rapid qualitative tests to be performed to monitor development and exposure proceses in photolithography and optical recording. For low modulated phase gratings there is a linear relationship between its square modulation (ϕ^2) and the first-order diffraction intensity, whatever the grating shape. By adequately selecting the value of ΔE (Fig. 1) some singular points on the response curve may be easily identified by simple visual comparison of the diffraction of a distant point light source. In this way and using an adequate layout on the sample (some slits are located so that a grating of amplitude ΔE may be superimposed with different preexposures E), the maximum derivative (most sensitive point), the threshold, and the saturation limits may be identified by simply comparing the brightness of the first-order diffraction image of a distant light source appearing in the successive film areas These data are useful for optimizing exposure and development processes. We successfully employ this method for optimizing (development and exposure times) a modified developer (the already mentioned solution of NaOH) for the AZ-1350B resist.



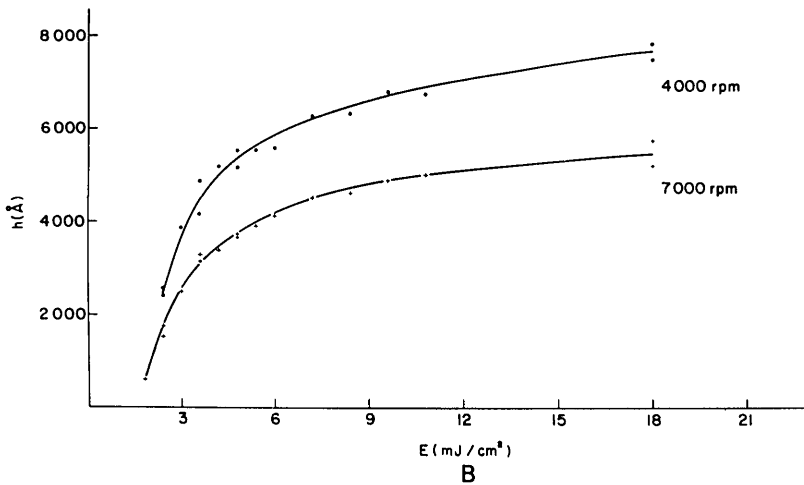


Fig. 3. Response curve for KMR-747 negative resist. The derivative curve is shown as measured for a film coated with a spinner at 4000 rpm (A). The integral response curves were independently measured by recording full modulated lamellar gratings and measuring their diffraction spectra (B).

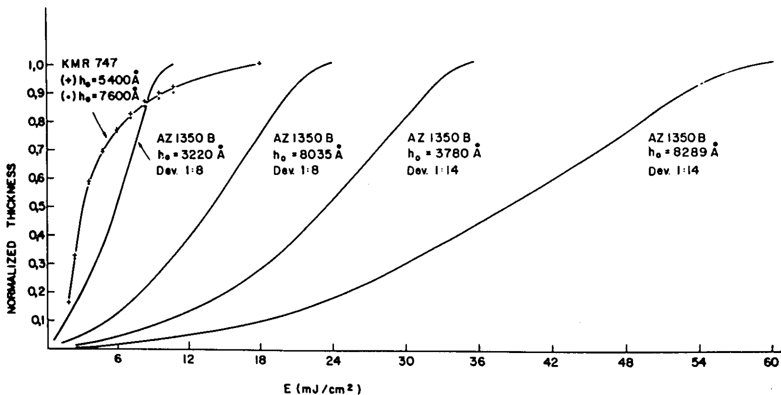


Fig. 4. Normalized response curves. The curves appearing in Figs. 2 and 3 are now normalized on their respective h_0 and represented here for comparison.

IV. Conclusions

The exposure of a low modulated pattern of light allows the response curve of a photosensitive film to be measured without accounting for nonlinearity. Exposure and development processes may also be optimized by a simple qualitative visual test which may be incorporated in routine work. This test is facilitated by the fact that the derivative response is directly available from experiment.

The method may also allow the response curve to be measured for large spatial frequencies and still meet the conditions for Fourier formalism,[7] which largely facilitates the handling of diffraction data. In this case a holographic recording setup is necessary, which will probably be limited by noise and stability considerations (vibrations, stray light, long-term thermal drift, etc).

In some situations, such as with KMR-747 negative photoresist, the integral curve is too indeterminate to be worth computing from derivative data. Anyhow, the derivative curve is as good a means of characterizing the photosensitive film as the integral curve itself. Some information is even better handled in its derivative form as is the case for selecting the most linear response range and choosing the most sensitive working point for that film.

A question arises whether data obtained using low modulated gratings may be comparable or not with the data measured with deep modulated gratings. In fact, wet development may behave differently in both cases at least for high spatial frequencies. We did not compare both results because this paper is limited to gragings of low spatial frequencies (f = 10 lines/mm) where we do not expect differences to appear. Applications using low modulation recording such as spatial multiplexing, for example, may probably better profit from data obtained from this derivative technique than from conventional methods. The response curve of some photoresist films was measured using this method, but it may certainly apply to other types of photosensitive material as well.

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LIFEDANCE

by Deborah Taylor

Some say the time of beauty is dead,
gone with clean air and old morality.
Our modern times are cold and graceless, they say,
moving sullenly through boredom and triviality:
All plastic and microchips; sterile and sanitized.

But the soft gray wariness of a squirrel regards me
through dappled leaves unfolding to embrace their lover,
the sun, as I enter a building of polished stone.
Here I see, by aid of man's work, the ageless
bacteria moving through their endless dance.
They do not know that I join them,
sharing the figures unknowingly, but with sure steps.

For I hear the music of the spheres, their crystal notes,
I pipe the hollow tones of the Fair Folk;
my bow reveals the song of the sea nymphs.
All to accompany a dance that begins in a helix,
but whose ending is unknown.

Contributed by Karl A. Stetson