FABRICATION OF PHOTORESIST MASKS
FOR SUBMICROMETER SURFACE RELIEF GRATINGS

Lifeng Li, Mai Xu, George I. Stegeman, and Colin T. Seaton*

Optical Sciences Center
University of Arizona, Tucson, Arizona 85721

ABSTRACT

A method of fabricating photoresist grating masks with Shipley's 1400 series positive photoresist by monitoring the negative first-order diffraction efficiency during the photoresist development is presented. The relationship between the monitoring curve and the mask profile evolution is examined.

1. INTRODUCTION

Periodic corrugations, or surface relief gratings, have many important applications in integrated optics, such as waveguide beam couplers and distributed feedback reflectors, and new applications continue to appear. The demand for fabricating good submicrometer gratings is ever increasing.

For integrated optics applications, gratings are generally made by the holographic technique, that is, by exposing photoresist to the interference pattern of two laser beams. Figures 1(a) and (b) show two possible photoresist grating profiles. Surface relief gratings etched into substrates or waveguides, as in Figure 1(c), are usually preferred to photoresist gratings because they are more durable, and the latter are used only as etching masks. During etching, the substrate or waveguide material exposed to the ion beam or chemical solution is etched away, but that covered by the remaining photoresist remains intact. To assure a successful etching, the photoresist between the peaks of the photoresist gratings must be completely removed from the substrate surface. It is also important that an optimum aspect ratio, the ratio of the width of the peak to the width of the trough [see Figure 1(b)], of the photoresist grating masks be obtained because it ultimately affects the profiles of the etched gratings.

Many papers have been published on photoresist grating fabrication.[1-4] However, most of these papers do not concern themselves with the fabrication of photoresist gratings as etching masks. Stepanov et al.[5] gave a very good prescription for grating mask preparation. Their emphasis is on the adjustment and control of the exposure time. In our opinion, exposure is an important step in the photoresist grating fabrication, but it is far more important to control the development process. The development comes after the exposure, and therefore overexposure or underexposure can be corrected by adjusting the development. In 1970, Beesley and Castledine[1] proposed a method to control the photoresist grating development, which was later used by Tsang and Wang[2] in the simultaneous exposure and development technique. This method monitors the negative first-order diffraction efficiency of the photoresist grating while it is being developed. Once the relationship between the grating profile and the diffraction efficiency as a function of development time is known, an optimum grating profile can be obtained by stopping the development at an appropriate time. Although this method proved very simple and effective for making holograms and diffraction gratings, Beesley and Castledine did not consider its application to

* Permanent Address: Changchun Institute of Physics, Academia Sinica, P.R.C.

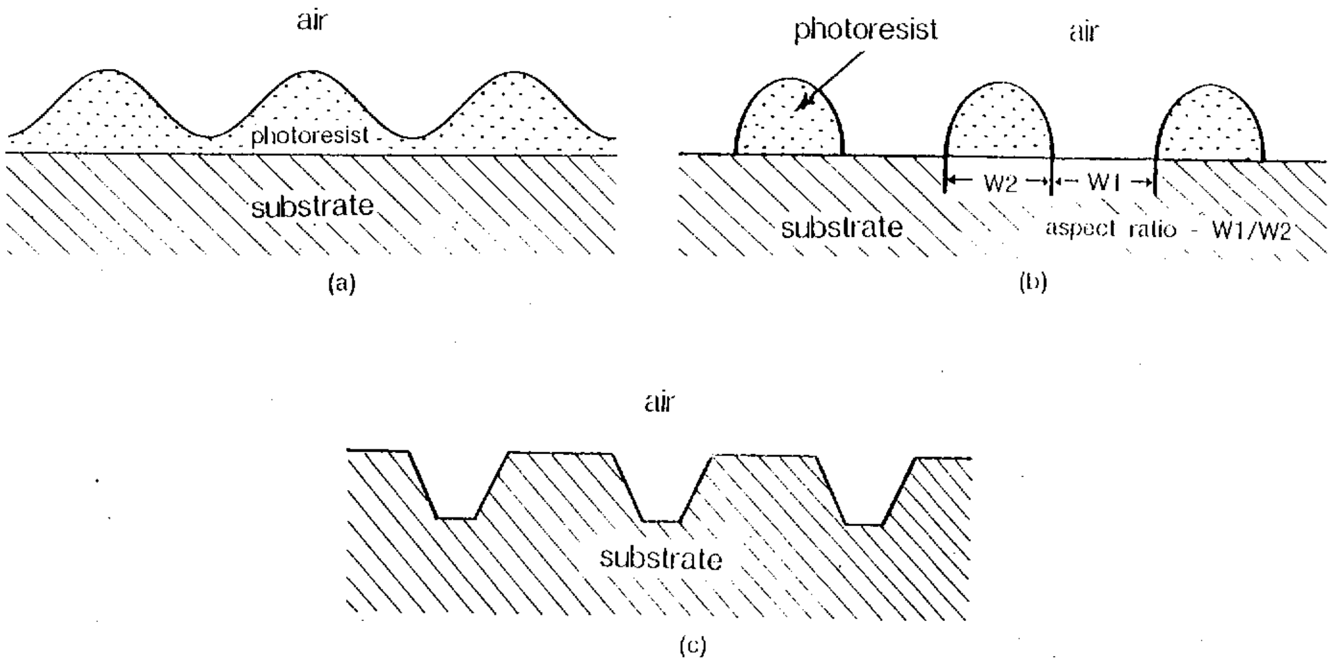


Figure 1. Schematic cross section of (a) a photoresist grating, (b) a photoresist grating mask, and (c) an etched grating.

the fabrication of grating masks, which has different fabrication requirements from those of grating holograms or diffraction gratings. In this paper, we use this method to investigate the control of the development in the fabrication of grating masks with Shipley's 1400 series photoresist. We first evaluate different monitoring configurations. Then we describe our experimental setup. Finally, by presenting scanning electron microscope (SEM) photographs of photoresist gratings and their monitoring curves, we discuss the relationship between the diffraction efficiency as a function of development time and the grating profile evolution during development, and show how it can be used to control grating mask development.

2. MONITORING CONFIGURATION

2.1. Choice of diffraction order

The diffraction order to be monitored should have good sensitivity to the grating profile change and should have strong enough intensity to be easily detected. The two zeroth diffraction orders do not provide enough sensitivity because, unless the photoresist grating grooves become very deep, the diffraction efficiencies do not change very much from their initial values. The two positive first orders, and the second and higher orders, do not have very high intensities, and, moreover, they may not even be propagating for short period gratings. Thus only the two negative first-order diffractions meet the requirements.

Moharam and Gaylord[9] and Moharam et al.[10] have shown theoretically and experimentally that, at the first-order Littrow mounting, as the photoresist grating groove depth increases, the transmitted negative first-order diffraction efficiency increases monotonically (to about 85%) until the ratio of grating depth to grating period reaches about 1.5. Our calculation using the integral formalism[11] comfirms this, and shows that the reflected negative first-order diffraction efficiency oscillates at a period of about $\lambda/2$. In our labortory, fused quartz substrates are most frequently used. Making gratings on fused quartz substrates does not require deep-groove photoresist grating masks because with C_2F_6 reactive ion etching, fused quartz has a much higher etch rate than does photoresist. It is sufficient to limit the photoresist thickness to about half or less of the grating period. As the grating groove depth increases during the initial phase of the development, the transmitted negative first-order diffraction efficiency remains in the monotonically increasing region. When the developer has etched to the substrate surface and the grating peak narrows, the efficiency decreases. So there is only one maximum in the monitoring curve and the correspondence between the curve and the grating profile evolution is unambiguous. However, the oscillatory nature of the reflected negative first-order diffraction efficency may cause confusion in practice. Therefore, whenever possible, we have used the transmitted negative first order for monitoring. For opaque substrates, of course, only the reflected negative first order can be used.

2.2. Choice of incident angle

For the monitoring beam incident angle we use the first-order Littrow mounting at which the negative first-order diffraction in reflection propagates antiparallel to the incident beam. This mounting is experimentally easy to implement,gives high diffraction efficiency, and, more important, works for shorter grating periods than normal incidence does. At this mounting we have $\sin\theta = \lambda/(2n\Lambda)$, while at the normal incidence $\sin\theta = \lambda/(n\Lambda)$, where θ is the diffraction angle, λ is the monitoring laser wavelength, Λ is the grating period, and n is the refractive index of the developer. Thus, the minimum period that can be monitored at the Littrow mounting is half the period at the normal incidence.

2.3. Choice of monitoring light source

Ideally, the monitoring light source wavelength should be in the visible to make the monitoring easy, short enough to allow at least one nonzero diffracted order, and long enough to be inactive to the photoresist. A HeNe laser is usually a good choice. When the grating period is less than $0.6328\ \mu m/(2*1.33) = 0.24\ \mu m$, where 1.33 is the estimated refractive index of diluted developer, a HeNe laser does not produce any nonzero propagating orders, and a shorter wavelength light source must be used. However, a photoresist is sensitive to green or blue light, so a probe beam with wavelength shorter than green light must be attenuated before it is incident on the grating being developed.

Although the grating diffraction efficiency depends on the beam polarization when the wavelength and grating period are comparable, no significant effects on development monitoring have been observed. Therefore, in this paper, an unpolarized HeNe laser is used, unless otherwise specified.

3. EXPERIMENTAL SETUP

Figure 2 is a schematic diagram of our optical system for holographic exposure.[6-8] Briefly, a HeCd laser beam is spatially filtered, expanded, and collimated. Half the collimated beam is incident directly on the photoresist film and half incident on the mirror and then folded back onto the photoresist film, creating a periodic exposure inside the photoresist film.

Figure 3 is a schematic diagram of our development-monitoring setup. A HeNe laser beam is incident on the developing photoresist grating. The grating is clamped in a holder which is mounted on a rotator so that the incident angle can be adjusted while the incident beam is kept on the grating. The rotator is mounted on top of a cylindrical quartz cell which contains the developer. A developer circulating system is also included to keep the photoresist grating in contact with fresh developer during development. The negative first-order diffraction intensity is measured by a photodiode and recorded by a chart recorder. Our grating holder and development-cell assembly are designed so that the grating holder can be inserted into the development cell quickly to start development and direct the negative first-order diffraction precisely onto the detector. It can also be quickly pulled out of the development cell and put into a

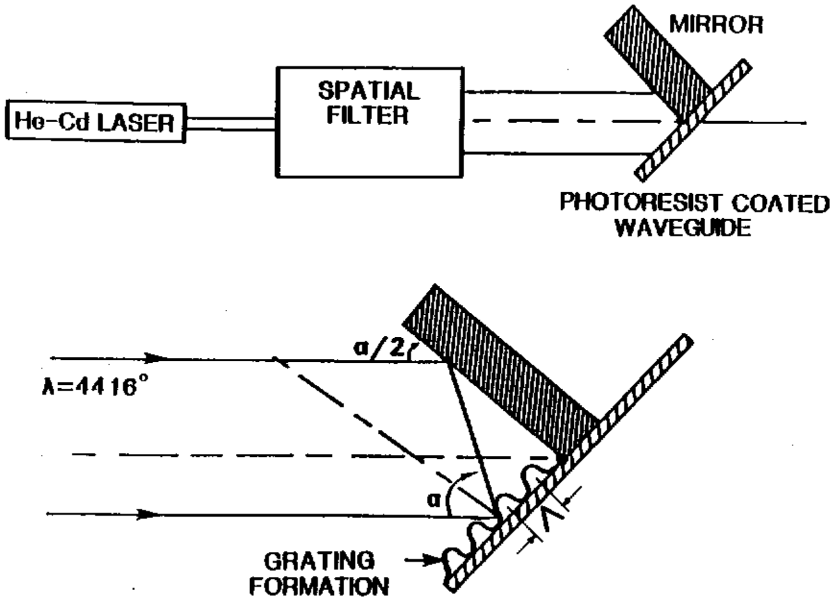


Figure 2. Holographic exposure setup.

$$\Lambda = \frac{\lambda}{2 \sin\frac{\alpha}{2}}$$

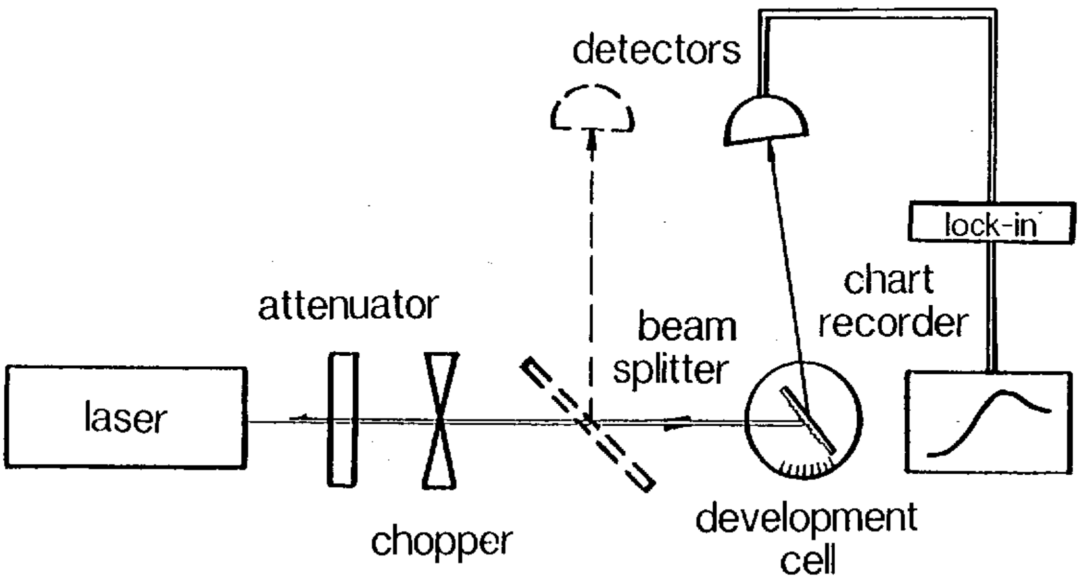


Figure 3. Development monitoring setup.

beaker containing fresh water to stop development. For a reflection grating, a beamsplitter can be conveniently added in front of the development cell to extract the negative first-order diffracted beam. The beam attenuator, chopper, and lock-in amplifier are needed only when the HeCd laser beam is used as the monitoring beam. The beam attenuator weakens the HeCd laser beam to a safe level and the chopper and lock-in amplifier detect the extremely weak negative first-order diffraction.

4. RESULTS AND DISCUSSION

Some examples demonstrate our results. Figure 4 contains SEM photos of photoresist gratings with different development times and their monitoring curves. They refer to the following conditions: Shipley 1400-17 photoresist, Shipley developer 351, developer concentration 17%, photoresist thickness 0.15 μm, grating period 0.6 μm, exposure beam intensity 0.5 mW/cm^2, and exposure wavelength 4416 Å. The photoresists after coating on the substrates were soft baked for 30 minutes at 90°C before exposure. Figure 5 shows grating profiles of another group and monitoring curves under the same conditions as those for Figure 4, except that the grating period is 0.4 μm and the developer concentration is 12.5%. Figure 6 shows a 0.2-μm-period photoresist grating mask and its monitoring curve. The monitoring is done with a TE polarized (E vector parallel to the grating grooves) HeCd laser beam. Figure 7 is a monitoring curve for a 1.5-μm-period photoresist grating on an InSb substrate monitored with the reflected negative first-order diffraction. The photoresist thickness is about 0.2 μm. The photoresist grating was intentionally developed for a long time to obtain a curve of a complete development process. The monitoring curves are reproduced from the chart recorder recordings. The vertical scales of the monitoring curves are arbitrary but consistent for each group and proportional to the diffraction efficiency. The vertical scales in some of the photos are out of proportion because of screen drifting while the photos were taken.

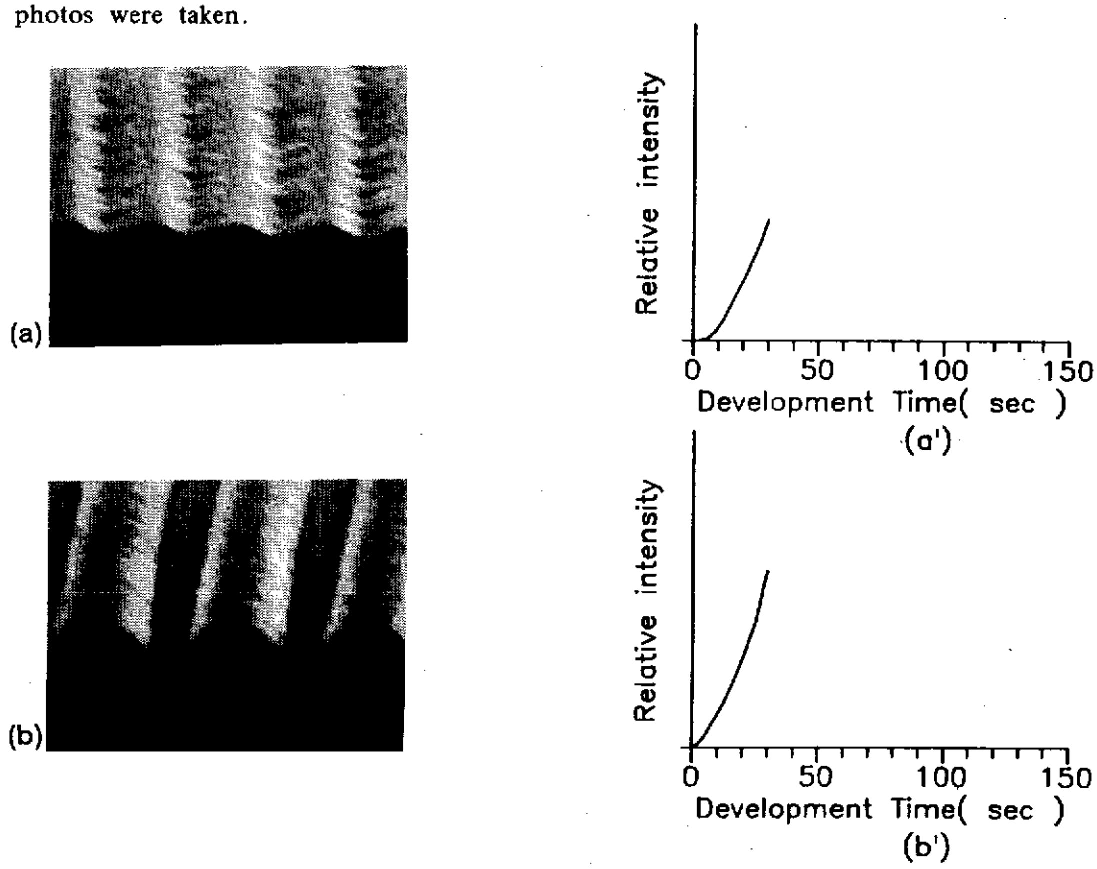


Figure 4. Scanning electron micrographs of photoresist grating masks with different development times(a through h) and their corresponding monitoring curves (a' through h'). The grating period is 0.6 μm and the developer concentration is 17%.

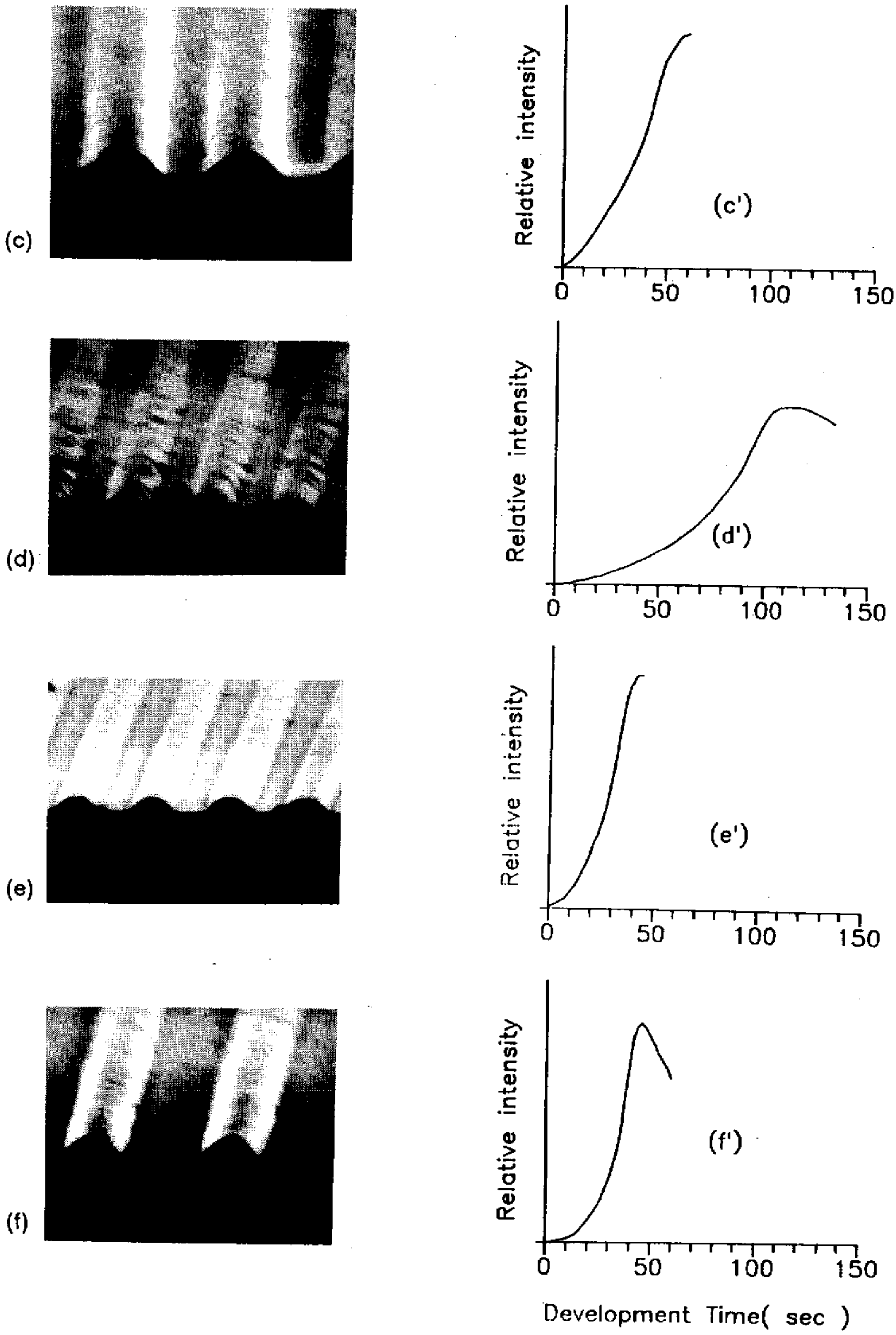
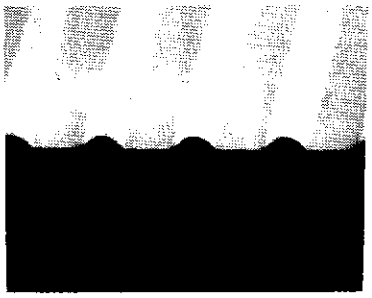
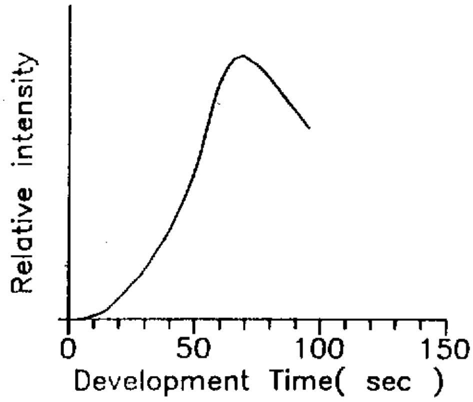


Figure 4 (cont'd). Scanning electron micrographs of photoresist grating masks with different development times(a through h) and their corresponding monitoring curves (a' through h'). The grating period is 0.6 μm and the developer concentration is 17%.

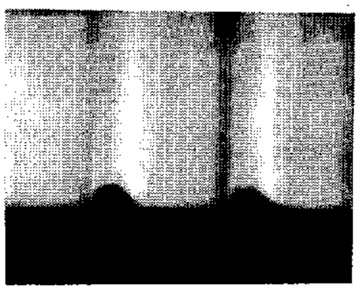
(g)

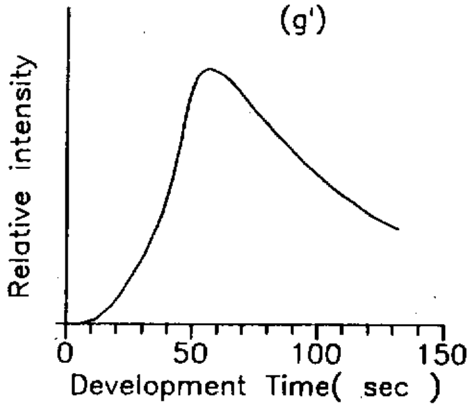




(g')

(h)





(h')

Figure 4 (cont'd). Scanning electron micrographs of photoresist grating masks with different development times(a through h) and their corresponding monitoring curves (a' through h'). The grating period is 0.6 μm and the developer concentration is 17%.

(a)

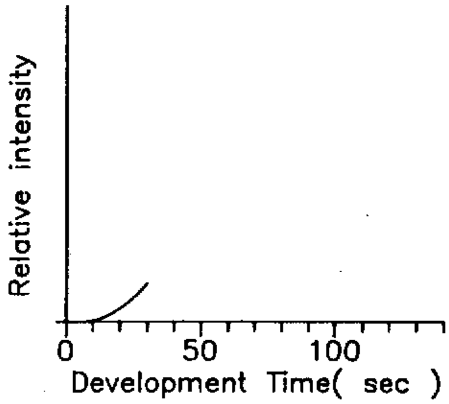


Fig. 5(a')

Figure 5. Scanning electron micrographs of photoresist grating masks with different development times (a through f) and their corresponding monitoring curves (a' through f'). The grating period is 0.4 μm and the developer concentration is 12.5%.

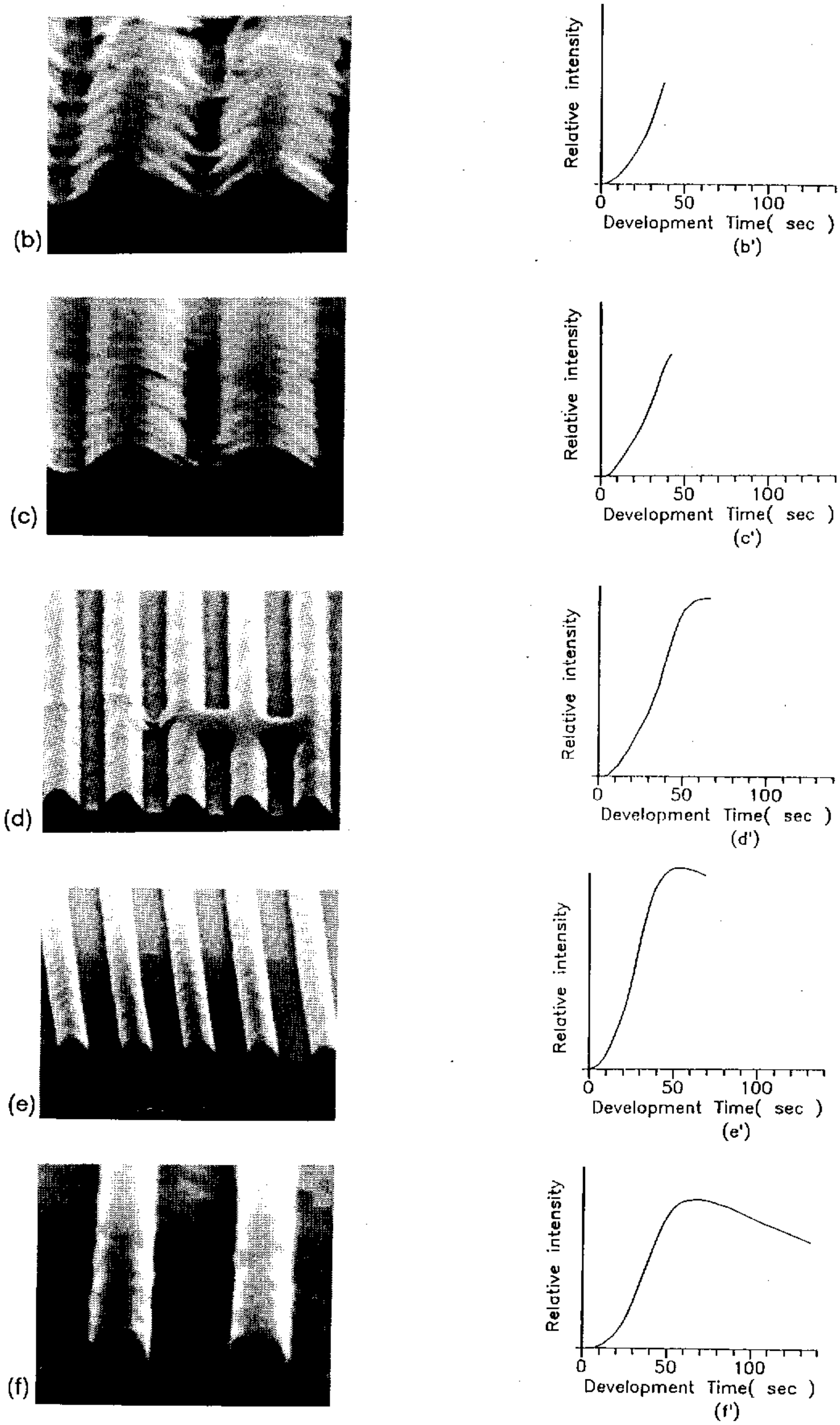


Figure 5 (cont'd). Scanning electron micrographs of photoresist grating masks with different development times (a through f) and their corresponding monitoring curves (a' through f'). The grating period is 0.4 μm and the developer concentration is 12.5%.

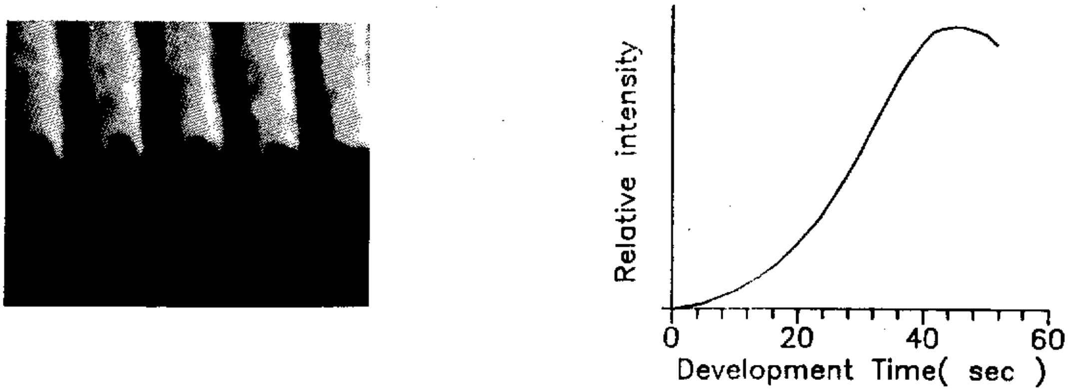


Figure 6. Scanning electron micrograph of a 0.2-µm-period photoresist grating mask and its monitoring curve.

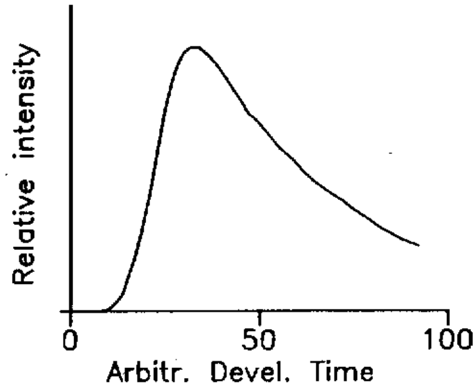


Figure 7. Monitoring curve for a 1.5 µm period photoresist grating mask on an InSb substrate.

We make the following observations:

1) At the beginning of the development process, the photoresist in the grating grooves develops away quickly, and the monitoring curves rise steeply with positive second-order derivatives. When the developer touches down to the substrate surfaces, the grating groove depths cease to increase and the grating peaks narrow. Meanwhile the monitoring curves still rise but begin to bend over, and the second-order derivatives become negative. At some points the monitoring curves reach their maxima and begin to fall with slopes less than the slopes of their rising edges.

2) The substrate surface is exposed to the developer in the middle section of the rising edge of the monitoring curves; see Figures 4 and 5 (a)-(a') and (b)-(b'). The maximum diffraction efficiencies occur roughly when the area of the cross section occupied by the remaining photoresist is equal to the area that has been etched away; see, for example, Figures 4(c) and (c'). The 1:1 aspect ratio occurs shortly after the monitoring curves pass their peaks; see Figures 4 (e)-(e') and (f)-(f') and Figure 5 (d)-(d') and (e)-(e').

3) It is the position on the monitoring curve, not the absolute development time, that provides a measure of the photoresist grating development. For example, grating 4(d) had a much longer development time than grating 4(c), but it has a profile similar to grating 4(c). The big change in the development rate is unknown. Evidently, without the monitoring technique, grating 4(d) would have been considerably underdeveloped.

4) The monitoring curves do not have the same maximum and do not reach their maxima at the same time, even for the samples with the same processing conditions, because of the lack of uniformity in the photoresist processing. The shapes of these curves are also not exactly reproducible because of the differences in developer concentrations, substrate reflectivities, grating periods, and photoresist processing. However, the shapes of the monitoring curves and the correspondence between the curves and grating profiles are all qualitatively the same.

Once the ralationship between a monitoring curve and the grating profile evolution is known, development control is easy. For example, to obtain an aspect ratio of less than, equal to, and greater than 1.0, the development should be stopped before, shortly after, and long after the monitoring curve passes its peak, respectively. This has been a rule of thumb in our daily grating fabrication, and the results are very good and consistant.

The relationship between the monitoring curve and the grating profile evolution holds as long as the monitoring is done in the monotonically increasing region of the grating diffraction efficiency, i.e., as long as the grating's groove depth-to-period ratio is less than $\cong 1.5$ if the transmitted negative first order is used.

One shortcoming of this method is that it is difficult to judge when to stop the development if a small aspect ratio is desired. In this case the development should be stopped before the diffraction peak is reached, and the judgement has to be made without referencing the location of the peak.

The method we have described is short of being quantitative. With this method, it is easy to obtain an approximate aspect ratio, but not an exact one. To move from being qualitative to being quantitative, a more accurate photoresist processing control prior to the development is required. Theoretical modeling of the exposure and development may also help.

This paper has focused attention on the control of the development time. This does not mean that the exposure time is not important. However, our experience shows that as long as the exposure time is not too far from "optimum," an optimum grating profile can always be obtained by adjusting the development time (without fixing the development time it is impossible to define an optimum exposure time; by "optimum," we mean the optimum exposure time for a reasonable development time, for example, 30 or 60 seconds).

5. CONCLUSIONS

The method of controling photoresist grating development by monitoring grating diffraction efficiency has been applied to the photoresist grating mask fabrication. With this method, grating masks with clean troughs and different predetermined aspect ratios can be made reliably and repeatably.

6. ACKNOWLEDGEMENTS

The authors are grateful to Mr. Kevin Erwin for his technical assistance. This research was supported by the Optical Data Storage Center and by the Office of Naval Research.

7. REFERENCES

1. M. J. Beesley and J. G. Castledine, "The use of photoresist as a holographic recording medium," Appl. Opt. 9(12), 2720-2724 (1970).

2. W. T. Tsang and S. Wang, "Simultaneous exposure and development technique for making gratings on positive photoresist," Appl. Phys. Lett. 24(4), 196-199 (1974).

3. S. Austin and F. T. Stone, "Fabrication of thin periodic structures in photoresist: a model," Appl. Opt. 15(4), 1071-1074 (1976).
4. H. Werlich, G. Sincerbox, and B. Yung, "Fabrication of high efficiency surface relief holograms," J. Imag. Technol. 10(3), 105-108 (1984).
5. S. S. Stepanov, V. A. Sychugov, and T. V. Tulaiikova, "Method for preparing photoresist grating masks," Sov. J. Quantum Electron. 10(4), 483-486 (1980).
6. A. Malag, "Simple interference method of diffraction grating generation for integrated optics by the use of a Fresnel mirror," Opt. Commun. 32(1) 54-58 (1980).
7. M. Xu and Y. Li, Acta Scientiarum Naturalium Universitatis Jilinensis(China), No. 4, 1982, p 65.
8. M. Xu, R. Moshrefzadeh, U. J. Gibson, G. I. Stegeman, and C. T. Seaton, "Simple versatile method for fabricating guided-wave gratings," Appl. Opt. 24(19), 3155-3161 (1985).
9. M. G. Moharam and T. K. Gaylord, "Diffraction analysis of dielectric surface relief gratings," J. Opt. Soc. Am. 72(10), 1385-1392 (1982).
10. M. G. Moharam, T. K. Gaylord, G. T. Sincerbox, H. Werlich, and B. Yung, "Diffraction characteristics of photoresist surface-relief gratings," Appl. Opt. 23(18), 3214-3220 (1984).
11. D. Maystre, "Integral methods," in *Electromagnetic Theory of gratings*, R. Petit, ed., Topics in Current Physics, Vol. 22, pp 63-100, Springer-Verlag, Berlin (1980).