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LITHOGRAPHIC CHARACTERIZATION OF A RAPID
AMMONIA CATALYZED IMAGE REVERSAL PROCESS

by

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ABSTRACT

A rapid ammonia catalyzed image reversal process has been developed using active kinetic control with a throughput of 50 wafers in 15 minutes. Lithographic characterization of this process demonstrate that 0.5 μm lines and spaces can be consistently resolved using a g-line stepper equipped with a 0.42 NA lens. However, the characterization also underlined deficiencies for printing various 2-dimensional features. Of these, line truncation and proximity effects may limit the utility of image reversal for enhancing resolution unless the mask can be suitably compensated.

We modeled the image reversal process using the PROLITH simulation tool[1] to understand the observed enhancement mechanism. Modeling results suggest that overexposures are necessary to achieve resolution enhancement. Furthermore, image reversal optical processes are fundamentally different than positive when partially coherent light is used for the initial exposure.

INTRODUCTION

Ammonia catalyzed image reversal has been proposed as a general method to enhance the lithographic performance of an exposure tool without resorting to multilevel enhancement schemes[2,3]. For example, Ziger and Reightler modified a commercial image reversal process and were able to resolve 0.625 μm linear features with a 0.35NA lens[4]. Results from this study showed that the thermal history during the ammonia bake drastically affected both process resolution and latitude. Furthermore, process reproducibility is affected if the thermal history varies from wafer to wafer and lot to lot. This was attributed to varying extents of thermal degradation of the photoactive compound (PAC) during the reversal bake which causes developing

nonuniformities. Ziger and Reightler suggested that insuring thermal history uniformity from wafer to wafer and batch to batch is critical to reproduce the image reversal process. Furthermore, Ziger and Wolk suggested that thermal processing of resist materials should be kinetically controlled such that the extent of decomposition is maintained from batch to batch and wafer to wafer[5].

APPROACH

Kinetic Control

Kinetic control of the image reversal process requires knowledge of the reaction rates. To simplify complicated solid state kinetics, we assume that the unexposed resist thermally decomposes slower than the reversal reaction in the exposed regions. Consequently, maintaining the same extent of decomposition assures process reproducibility. Assuming first order decomposition kinetics and an Arrhenius temperature dependence, Equation (1) can be used to scale thermal processes such as image reversal:

$$\ln\frac{c_f}{c_0} = -A \int_{t=0}^{t} e^{-\frac{E_a}{RT}} \, dt \qquad (1)$$

To use Equation (1), we must first measure or estimate the Arrheniums activation energy, E_a, and pre-exponential factor A and measure the temperature history during the process. Image reversal is optimized over parameter space and SEM results are correlated to the estimated extent of reaction , c_f/c_o. Thereafter, the process is terminated at the same extent of reaction. Figure 1 shows the general kinetic control process as applied to the amine bake for ammonia catalyzed image reversal.

Since the amine bake is controlled by the measured thermal history, this method automatically compensates for run to run thermal variations, batch size differences and thermal loading

effects caused by different substrates.

PROLITH Modeling

PROLITH[1] is a versatile modeling program which has been used to study resist processes such as the effects of prebaking[6], standing waves[7], contrast enhancement[8], and postexposure baking[9]. PROLITH modeling enabled us to compare aerial images between standard processing and image reversal. Based on these comparisons we have postulated an enhancement mechanism for image reversal based on optical phenomena.

EXPERIMENTAL

A commercial STAR 2001 image reversal reactor was modified to implement kinetic control. The most significant changes were:

1. using anhydrous ammonia rather than ammonium hydroxide for the amine vapor source

2. adding a cassette loader and unloader

3. mounting thermocouple receptacles in the reactor

Figure 2 shows a picture of the apparatus designed to accomplish active kinetic control.

The ammonia source was switched to anhydrous ammonia for three reasons. First, anhydrous ammonia is a single component. Since ammonium hydroxide is a mixture of water and ammonia, the vapor concentration can vary with percentage of reservoir fill. If there is a small leak in the source container, then the ammonia concentration can vary from day to day. Secondly, ammonium hydroxide is potentially corrosive to metals such as aluminum raising reliability concerns. Finally, since anhydrous ammonia is a compressed gas, process pressure can be easily varied. However, the difficulty with utilizing anhydrous ammonia is the hazard of using NH_3 in the lithography room. To implement NH_3 and avoid the expense of piping from

outside, the apparatus was equipped with a fully vented lecture bottle cabinet.

Adding a cassette loader was important so that wafers could be automatically removed after the desired extent of reaction. In addition, thermo-couple receptacles were mounted inside the reactor to allow convenient temperature monitor-ing. These thermocouples were interfaced to a HP-9816 computer via a HP-3497A data acquisi-tion/control system. Extensive thermal monitor-ing was done to insure adequate temperature history uniformity. Baffles were required to optimize the thermal uniformity. Figure 3 illustrates the temperature profile history of a baffled 25 wafer cassette during an image reversal run.

Aside from the amine bake, commercial equipment was used for all other steps required for ammonia catalyzed image reversal. Initial exposures were done on a Nikon NSR-1505G45A3 0.42NA, g-line stepper. Resist films were spun and prebaked using GCA Wafertrac equipment. For this study, resist films were 1.4 μm of Hunt 204. Flood exposures were done on a Suss MA-56 broad band proximity printer. Immersion developing was done using 1:1 LSI developer.

LITHOGRAPHIC RESULTS

Process Optimization

Statistically designed experiments were used to first optimize and then characterize the litho-graphic performance of the batch ammonia catalyzed image reversal process. Desired attributes of this process were:

1. Rapid ammonia bake

2. Minimum resolution at relatively low overexposures

3. Maximum depth of focus

4. Verticle wall profiles

Using active kinetic control, the total ammonia bake time was decreased to about 18 minutes/ 50 wafer batch. This is 2-10 times faster than prior ammonia bake times for batch processing. Active kinetic control was critical towards decreasing process bake time since wafer tem-perature and estimated kinetics are constantly monitored. Consequently, higher oven tempera-tures could be used.

Relatively low exposure doses were desired for this process to minimize any stepper throughput loss. However, it was not possible to resolve 0.5 μm features without using an exposure dose of at least 1 second. Consequently, we were not able to achieve minimum resolution (0.5 μm) without resorting to exposure energies about 5-6 times standard exposures.

Figure 4 shows SEM results of 0.5 μm packed lines and spaces resolved using a 0.42 NA, g-line stepper under conditions which provided the best linearity for mask size versus feature size (Figure 5). The depth of focus for resolving these 0.5 μm lines was about ±0.75 μm.

Proximity Effects

In this study, it was desired to quantify various proximity effects such as the measured differ-ences between packed and isolated lines for the same mask feature size and truncation effects. It was seen that the processing conditions strongly affected these proximity affects. However, under the best conditions, the linewidths discrepancy between packed and isolated features was not significant above 0.6 μm (see Figure 4). How-ever, at 0.5 μm, this difference was 20% of the nominal linewidth.

Line truncation was a proximity effect which was most dependent on the mask feature size. Figure 6 shows data from 0.5-0.8 μm. At 0.5 μm, the average truncation was about the same as the nominal linewidth.

IMAGE REVERSAL MODELING

High resolution optical lithography processes primarily employ positive tone photoresists. It is not obvious why reversing their tone through image reversal should yield improved resolution. However, a closer examination reveals that negative photoresist processes may be fundamentally different from a positive process depending on the nature of the imaging system.

For incoherent light, aerial images of lines and spaces are complementary. That is, if the tone of the mask is exactly reversed, then the resulting aerial images for these two masks will be related by:

$$I_{(x)}^{pos\ tone} = 1 - I_{(x)}^{neg\ tone}. \qquad (2)$$

where x is the relative horizontal distance. Furthermore, the relative intensity always exhibits an inflection point at the mask edge with an intensity of 0.5. Thus, for incoherent illumination, there is no fundamental optical difference between positive and negative tone photoresist processes.

However, when partially coherent illumination is used in the projection system, as is done in all commercial projection tools, the complimentary nature of lines and spaces no longer exists. Shown in Figure 7 are aerial images of an array of 0.9 μm of equal lines and spaces for various coherence factors. Note that the shape of the aerial image for the partially coherent source is significantly different under the clear area of the mask than under the opaque area. Since the behavior of a lithographic system is strongly dependent on the shape of the aerial image, a negative process will behave differently from a positive system for partially coherent imaging.

There are other differences between standard positive processing and image reversal such as the overexposures which are required to achieve minimum resolution. To better understand these differences, a simple model was used. First we assume that the image reversal reaction is complete, that is, all carboxylic acid exposed initially is converted to an insoluble species, m_r. Second, we assume that no thermal degradation occurs during the amine bake, and third, that the subsequent flood exposure exposes all remaining PAC. Under these assumptions, the distribution of m_r, is related to PAC distribution from standard processing by:

$$m_r(x,z) = 1 - m(x,z). \qquad (3)$$

PROLITH was used to generate m(x,z) which could then be transformed into $m_r(x,z)$. Shown in Figure 8a are the calculated latent images for 1.0 μm lines and spaces for different exposure energies. The exposure energy needed to properly define the features will depend on the development properties of the resist. A typical positive resist requires an exposure of about 150 mJ/cm². Shown in Figure 8b are the reversed latent images $m_r(x)$ corresponding to the PAC distributions of Figure 8a and calculated using Eq. (3). Again, the necessary exposure level will depend on the development properties of the reversed photoresist. We assume, for the sake of comparison, that the development properties of the reversed resist are equivalent to that of the standard positive resist. Then the proper exposure for the image reversed resist should yield a latent image which has the same PAC concentration near the mask edge as the standard processing. By examining Figure 8b, we see that an initial exposure of 600 mJ/cm² is required to provide such a latent image. Thus, by assuming similar development properties between the standard and reversed photoresists, approximately a four-fold exposure increase is required to accomplish image reversal for the same resolution. This increase in exposure is due to the practical constraint that typical photoresist development properties put on the magnitude of the latent image.

Although the magnitudes at the mask edge for $m(150 \text{ mJ/cm}^2)$ and $m_r(600 \text{ mJ/cm}^2)$ are equivalent, their gradients are not. In particular, $\partial m_r/\partial x$ is significantly greater than $\partial m/\partial x$ at the mask edge. This increase is a direct result of the higher exposure energy used for image reversal[10]. An improved PAC gradient results in improved process latitude. Thus, image reversal should exhibit improved performance due to the required higher exposure and the resulting improved latent image gradient at the mask edge.

The simple image reversal model of Equation (3) has been incorporated into the PROLITH simulation tool. The resulting image reversal model can be compared to experimental linewidth versus exposure data, as shown in Figure 9. As can be seen, experimental data can be represented very well by this model.

CONCLUSIONS

A novel kinetically controlled image reversal process was developed which consistently resolved 0.5 μm packed lines and spaces in 1.4 μm of resist using a g-line stepper equipped with a 0.42 NA lens. This process compensated for loading and batch to batch thermal variations.

Lithographic characterization of this process demonstrated that although resolution of an exposure tool can be extended, its general utility might be limited by severe proximity effects unless the mask can be suitable compensated. Overexposures between 5-10 times those required for standard positive resist processing were required to achieve minimum resolution.

The image reversal process was modeled using PROLITH. Results suggest that the coherence of the illuminating source affects the reversal process. Furthermore, analysis of the calculated latent images indicate that overexposures are inherent to the image reversal process. Overexposing the photoresist increases the PAC gradient at the mask edge leading to the observed enhancement phenomena.

REFERENCES

1. C.A. Mack, "PROLITH: A Comprehensive Optical Lithography Model," SPIE Proceeding 538: Optical Microlithography IV, pp. 207-220 (1985.

2. E. Alling, C. Stauffer, "Image Reversal of Positive Photoresist - A New Tool for Advancing Integrated Circuit Fabrication," SPIE Proceeding 539: Advances in Resist Technology and Procesing II, p. 194 (1985).

3. C. Hartglass, "Optimization of Image Reversal of Positive Photoresist," Proceedings of the 1985 Interface Conference on Microlithography, San Diego, CA (1985).

4. D.H. Ziger, J.W. Reightler, "Analysis of Factors Affecting Ammonia Catalyzed Image Reversal," KTI Microelectronics Interface '87, pp. 13-25 (1987).

5. D.H. Ziger, G.L. Wolk, "Thermal Processing of Resist Materials: A Kinetic Approach," Advances in Resist Technology and Processing V, 920, 220 (1988).

6. C.A. Mack, R.T. Carback, "Modeling the Effects of Prebake on Positive Resist Processing," Kodak Microelectronics Interface'85, 155-158 (1985).

7. C.A. Mack, "Analytical Expression for the Standing Wave Intensity in Photoresist," App. Opt., 25., 1958-1961 (1985).

8. C.A. Mack, "Contrast Enhancement Techniques for Submicron Optical Lithography," J. Vac. Sci. Tech., (in press).

9. C.A. Mack, "Advanced Topics in Lithography Modeling," Adv. Resist Tech. III, SPIE Proc 631, pp. 276-285 (1986).

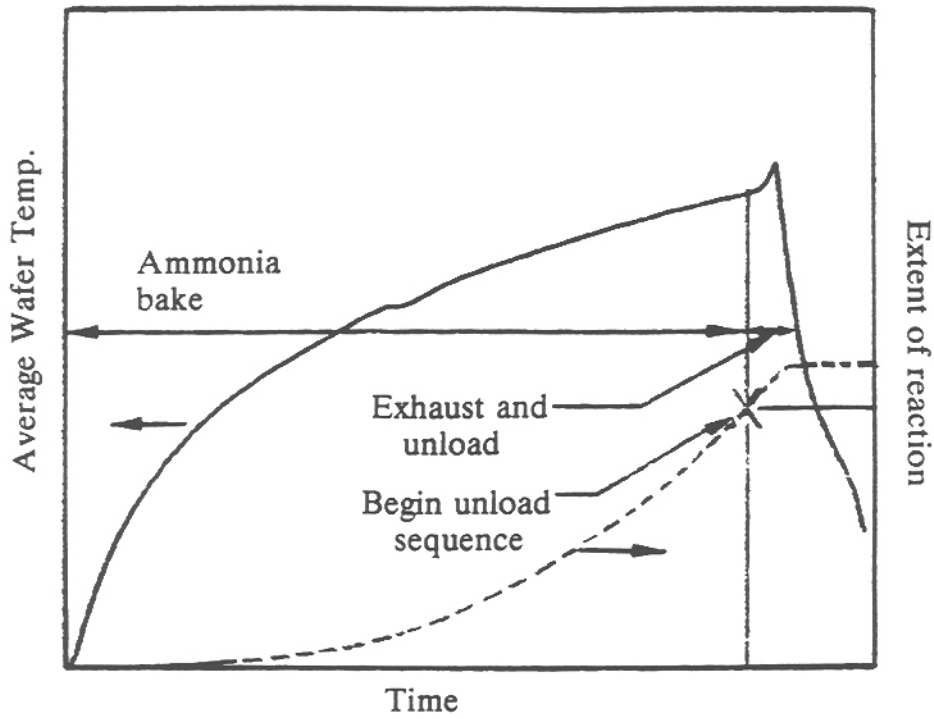10. C.A. Mack, "Photoresist Process Optimization," KTI Microelectronics Seminar Interface'87, 153-157 (1987)

Figure 1. The kinetically controlled image reversal process

Figure 2. Photograph of the AT&T image reversal equipment developed to accomplish active kinetic control.
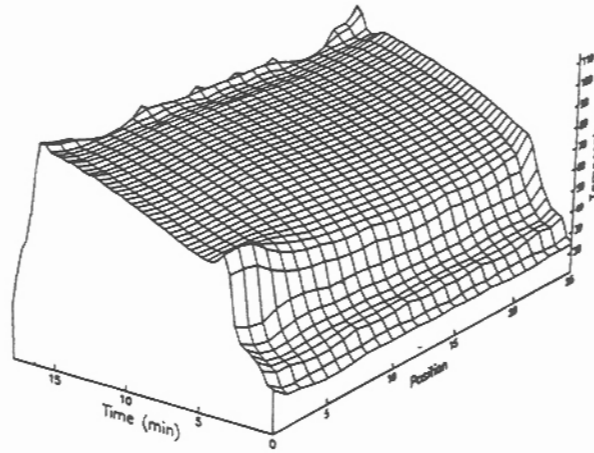
Figure 3. Measured temperature uniformity during the ammonia bake process across a cassette
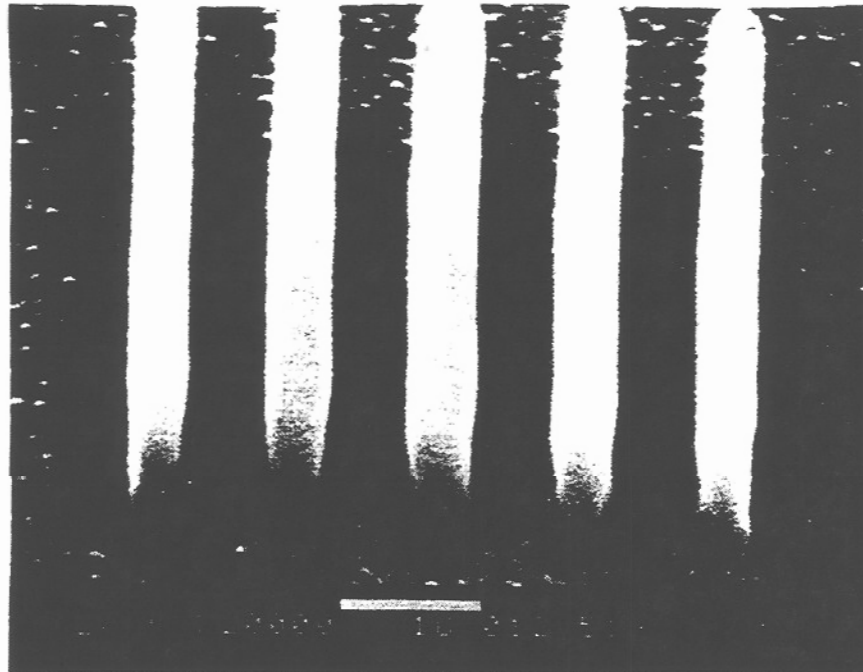
Figure 4. SEM photograph of 0.5 µm line and space features resolved with image reversal (0.42NA, g-line initial exposure).
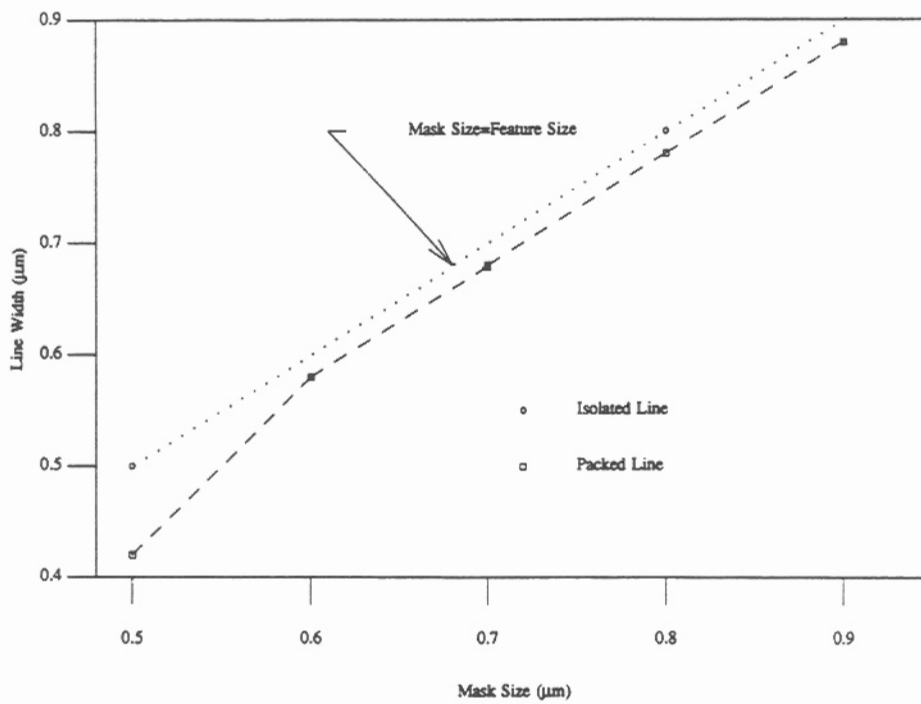
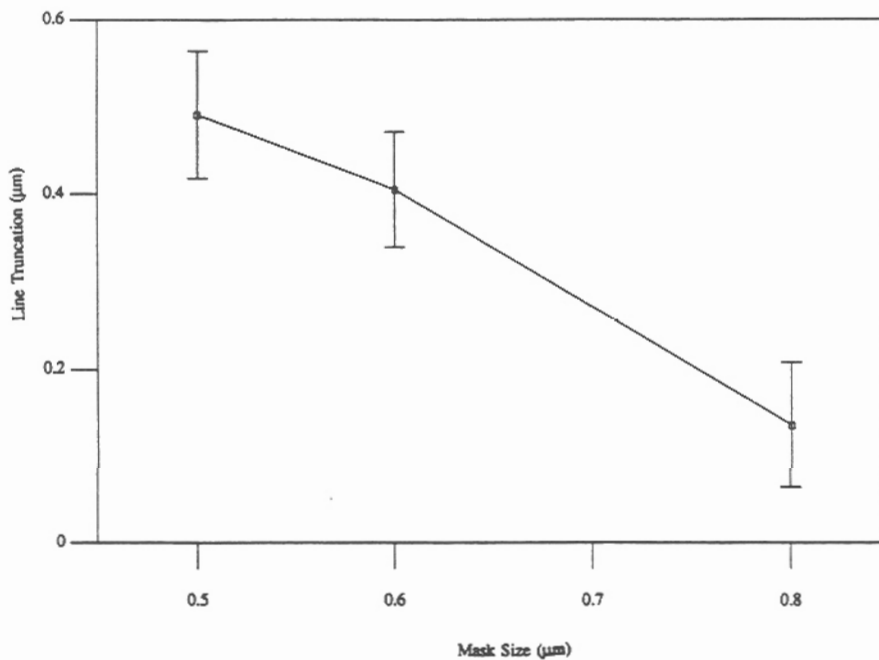Figure 5. Measured feature versus mask size.

Figure 6. Line truncation versus feature size (Error bars show estimate of one standard deviation in data caused by processing influences).
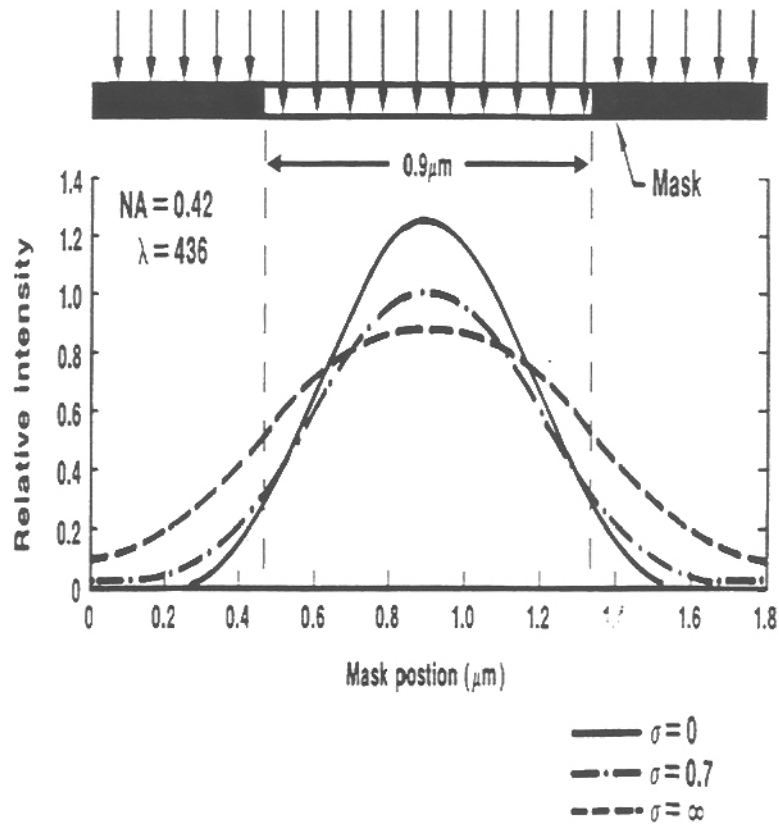
Figure 7. Aerial Images for incoherent (σ=∞), partially coherent (σ=0.7) and incoherent sources
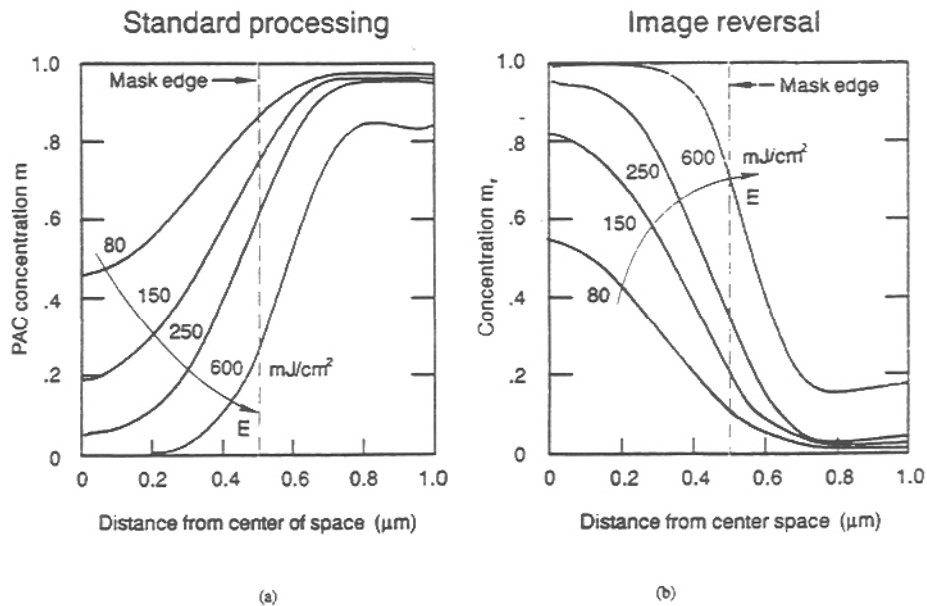
LATENT IMAGE MODELING

(a)

(b)

Figure 8. Latent images modeled with PROLITH for (a) standard processing and (b) image reversal
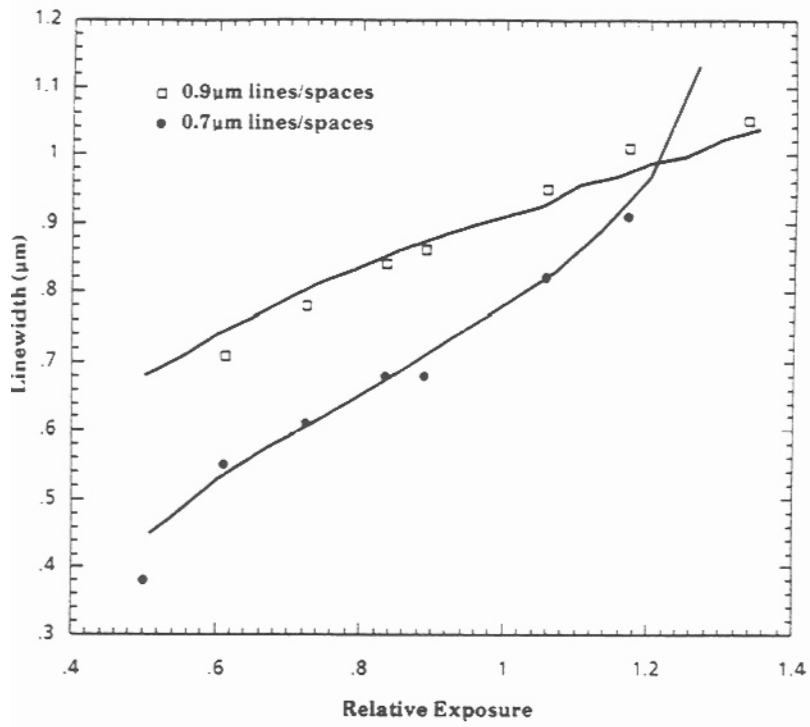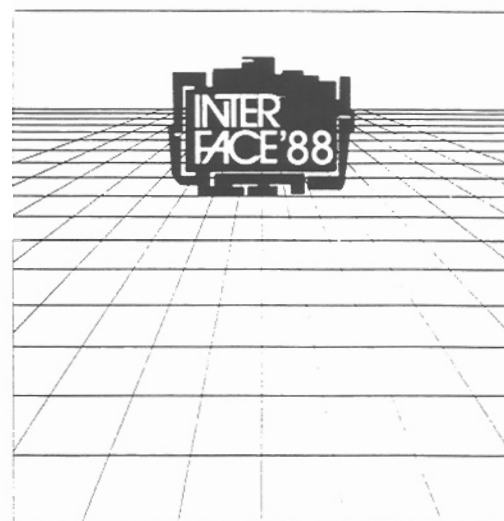
Figure 9. Experimental and correlated image reversal linewidth data
(Data points are experimental; lines are fitted to data)

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