INTERFACE '87

This paper was published in the proceedings of the
KTI Microelectronics Seminar, Interface '87, pp. 153-167.
It is made available as an electronic reprint with permission of KTI Chemicals, Inc.

Copyright 1987.
One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper are prohibited.

PHOTORESIST PROCESS OPTIMIZATION

by

Chris A. Mack
National Security Agency
Fort Meade, MD 20755

Chris A. Mack received his B.S. degrees in Physics, Chemistry, Electrical Engineering and Chemical Engineering from Rose-Hulman Institute of Technology in 1982. He joined the Microelectronics Research Division of the Department of Defense in 1982 and began work in optical lithography research. He has authored several papers in the area of optical lithography and has developed the lithography simulation program PROLITH. His current interests include lithography modeling photoresist characterization, and advanced resist processing.

In order to extend current optical lithography techniques to submicron feature sizes, it is important to optimize the processing of the photoresist. In practice, the "optimum" process is that which shows the greatest process latitude (i.e., linewidth control) and the best resist profile (i.e., sidewall angle) at the desired feature size. This paper will provide a theoretical method to optimize exposure latitude, develop latitude, and resist sidewall angle.

Beginning with the exposure process, it will be shown that the shape of the latent image (i.e., the concentration of exposed (or unexposed) photoactive compound) is strongly dependent on the exposure energy. In fact, there is only one exposure energy for a given resist/wafer system which produces the optimum latent image (with a maximum concentration gradient at the mask edge). There are several important implications of this finding. First, the common practice of adjusting exposure energy to compensate for process variations causes changes in the latent image, and thus changes in process latitude. Secondly, the common belief that there is reciprocity between exposure time and development time is false. Finally, by using a typical lithographic process as an example, it will be shown that the typical process significantly under-exposes and over-develops the resist, causing appreciable loss of process latitude.

Proceeding to the development process, it will be shown that the properties of development are usually dominant in determining process latitude (both exposure latitude and develop latitude). In fact, it is the development properties of many commercial resist systems which force a process to under-expose and over-develop. This type of photoresist is often referred to as a "high sensitivity" resist. It will be shown, however, that it is possible to choose a resist/developer system which takes advantage of the optimum exposure energy.

The analysis presented in this paper is based on the standard set of defining equations for the photolithographic process which takes into account absorption and bleaching. Equations are derived which allow for the optimization of the latent image, the resist sidewall angle, and the variation of linewidth with exposure energy. An "optimum resist" and an "optimum process" can be devised based on these equations.

Photoresist Exposure

The exposure of diazo-type novolak based positive photoresists can be described mathematically using the kinetics of the exposure reaction. The result is the well known first order rate equation [1],

$$\frac{\partial m}{\partial t} = -CIm \qquad (1)$$

where m is the relative concentration of unexposed photoactive compound (PAC), I is the intensity of the exposing radiation within the result, C is a rate constant, and t is the exposure time. The variables I and m are considered to be functions of two dimensions: x, the horizontal position; and z, the

depth into the photoresist. The point x=0 is arbitrarily set as the center of a symmetric mask feature and z=0 is the top of the resist. Equation (1) can be solved quite easily for the case of constant intensity, that is, when the photoresist does not bleach during exposure, The more gneral case requires more information about the intensity. The simplest case is when the photoresist is coated on a non-reflecting substrate so that the variation of I with depth into the resist is given by the Lambert-Beer law:

$$\frac{\partial ln(I)}{\partial z} = -(Am + B) \tag{2}$$

where A and B are constants which have been defined previously[2]. Equations (1) and (2) form two coupled partial differential equations with the following boundary conditions:

$$I(x,0) = I_0$$
$$m(x,0) = m_0 . \tag{3}$$

One can also see that these two boundary values are related by

$$m_0 = e^{-CI_0 t} \tag{4}$$

since I_0 does not change with time.

Equations (1) and (2) with boundary conditions (3) can be solved exactly[3] with the solution taking the form of an integral:

$$z = \int_{m_0}^{m} \frac{dy}{y[A(1-y) - Bln(y)]} \tag{5}$$

where y is a dummy variable for the purposes of integration, and

$$I = I_0 \frac{A(1-m) - Bln(m)}{A(1-m_0) - Bln(m_0)} \tag{6}$$

Unfortunately, the integral (5) can only be solved numerically. However, various related results can be obtained from the above equations.

Latent Image

Consider the variable m(x,z). This term is the chemical distribution of unexposed PAC (the exposed PAC is just 1-m), and is given the name *latent image*. As this name implies, m(x,z) is a reproduction of the aerial image within the resist. The questions arise, how can one define the qualtiy of the latent image and, given a suitable definition, is it possible to optimize the latent image? To answer the first question, experience with the aerial image can be used as a guideline for analyzing a latent image. The quality of an aerial image can be expressed in one of two ways. For a periodic pattern of lines and spaces, an *image contrast* can be defined as

$$contrast = \frac{I(center\ of\ space) - I(center\ of\ line)}{I(center\ of\ space) + I(center\ of\ line)} . \tag{7}$$

Although this definition is convenient, it is not the best indicator of image quality. The slope of the aerial image at or near the mask edge gives a good indication of image quality and can be applied universally to any pattern, not just periodic lines and spaces. Thus, we will now derive equations to determine the slope of the latent image (also called the PAC concentration gradient) and use these equations to optimize the latent image (i.e., maximize the slope).

Let us first consider the latent image at the top of the resist $m_0(x)$. To determine the slope one need only differentiate equation (4) with respect to x. After some algebra, one obtains

$$\frac{\partial m_0}{\partial x} = m_0 ln(m_0) \frac{\partial ln(I_0)}{\partial x} . \tag{8}$$

Several very interesting and important conclusions can be drawn from this simple equation. First, the slope of the latent image is not proportional to the slope of the aerial image, but to the slope of the log-aerial image. This dependency has been discussed previously[4,5] and will be shown to be important in nearly every aspect of lithographic imaging. Further, for a given aerial image, the slope of the latent image is a function of exposure. By plotting $m_0 ln(m_0)$, one can see that there is one value of m_0 which gives a maximum slope (Figure 1). It is easily determined that the maximum occurs at

$$m_0 = e^{-1} \approx 0.37 . \tag{9}$$

Thus, there is only one exposure energy which will maximize the latent image slope at some position x (e.g., at the mask edge), that which gives $m_0(x)$ equal to 0.37. The implications of this result are very important. First, there is one and only one exposure energy which gives the optimum latent image. Since, as will be shown later, process latitude is a function of the latent image slope, varying the exposure will vary the latitude of a photolithographic process.

Equation (8) applies only to the latent image at the top of the resist. Thus, the effects of bleaching and absoorption are not taken into account. To derive an expression analogous to equation (8) for the latent image slope at any depth into the resist, one must differentiate equation (5) with respect to x to get

$$\frac{\partial m}{\partial x} = \frac{\partial m_0}{\partial x}\left(\frac{m}{m_0}\right)\frac{A(1-m)-Bln(m)}{A(1-m_0)-Bln(m_0)}\ , \text{ or}$$
$$\frac{\partial m}{\partial x} = \frac{\partial m_0}{\partial x}\left(\frac{m}{m_0}\right)T = m ln(m_0)\, T\,\frac{\partial ln(I_0)}{\partial x} \qquad (10)$$

where T is the transmittance, defined as I(x,z)/I(x,0). Insight into the behavior of equation (10) can be gained by examining two special cases: A=0 and B=0.

The simple case of A=0 implies, from equation (2), that intensity is not a function of m and thus is constant with time. This is equivalent to saying the photoresist does not bleach. For such a case, equation (10) simplifies to

$$\frac{\partial m}{\partial x} = m\, ln(m)\frac{\partial ln(I_0)}{\partial x}\ . \qquad (11)$$

One can see that this equation is equivalent to equation (8) and has a maximum value when m is equal to 0.37. Although derived for the case of a non-reflecting substrate, equation (11) also applies to a reflecting substrate, with the restriction of a non-bleachable photoresist.

In a typical photoresist system, A has a value in the range of 0.5 μm^{-1} to 1.0 μm^{-1}. The value of B, however, is often a factor of ten less than this. Thus, the special case of B=0 is a good approximation of many photoresist systems. For this case, equation (10) reduces to

$$\frac{\partial m}{\partial x} = \frac{\partial m_0}{\partial x}\left(\frac{m}{m_0}\right)\frac{(1-m)}{(1-m_0)} = m ln(m_0)\frac{(1-m)}{(1-m_0)}\frac{\partial ln(I_0)}{\partial x}\ . \qquad (12)$$

Also, the integral (5) can be solved for this special case, giving

$$m = \frac{m_0}{m_0 + (1-m_0)e^{-Az}}\ . \qquad (13)$$

With the use of equations (12) and (13), the PAC gradient as a function of m can be determined (see Figure 2). Over a wide range of values of A times depth into the resist (Az), the optimum PAC slope is obtained for values of m in the range of 0.35 to 0.37. As can be seen in Figure 2, the PAC gradient is improved for larger bleaching effects (larger A). This has been referred to as the "built-in contrast enhancement effect" of resist bleaching.

One can see from Figure 2 that the maximum of the PAC gradient is fairly broad. Although the exact maximum may be about 0.36, the gradient is within 10% of the maximum over the range of about 0.2 to 0.5. For practical reasons it will be preferable to work with higher values of m (i.e., lower exposures), such as m=0.5 at the mask edge.

The above results can best be illustrated by way of example. Using the simulation program PROLITH[6,7], the latent image was calculated for typical g-line exposure of a one micron space on a non-reflecting substrate for different exposure energies. The results, shown in Figure 3, illustrate quite clearly the dependence of the latent image slope on exposure. Further, the optimum energy (200-250 mJ/cm^2) is two to three times greater than a typical exposure (80-100 mJ/cm^2). This exemplifies the important conclusion that a typical lithography process tends to under-expose and over-develop the photoresist.

Review of Development

The above analysis suggests that an improved latent image, and thus improved process latitude,

can be obtained by using a significantly higher exposure does than is typical. Without modification to the development process, however, such an exposure would result in severe photoresist loss, possibly washing out the patterns completely. Obviously, the development process must be tailored to take advantage of the optimum exposure energy. To see how this can be accomplished, a review of the properties of development is in order.

The best way to characterize the development process of a given resist/developer system is by knowing development rate as a function of PAC concentration. A typical development rate curve is shown in Figure 4. The shape of this curve is extremely important as it determines the imaging properties of the photoresist. As can be seen from Figure 4, the prominent shape is that of a threshold effect. Development rates for PAC concentrations above a certain value are quite low, while rates for concentrations below that value become high. In the case shown, the threshold effect occurs at about a value of $m \approx 0.5$ and this value is called the *threshold concentration*, m_{TH}. In a mathematical sense, the threshold PAC concentration can be defined as the inflection point of the development rate curve. In addition to m_{TH}, three other parameters must be defined in order to completely characterize the shape of the development rate curve. The two ends of the curve correspond to the development rate of completely exposed resist ($m=0$), called r_{max}, and the development rate of unexposed resist ($m=1$), r_{min}. Finally, the transition between high and low development rates can occur gradually or quickly. Some parameter, which can be called the *developer selectivity*, must be defined to describe this transition.

A kinetic development rate model has been introduced[8] which uses the four parameters given above to describe the shape of a development rate curve. Shown in Figure 5 are predicted curves for three different values of the developer selectivity parameter n.

Given the basic shape of the development rate curve, one can qualitatively determine how development interacts with the latent image to give a resist profile. Using the example of a space, development proceeds quickly in the center of the space where low values of m give high development rates. For this to be true, the exposure in the center of the space must be such that the values of m are less than m_{TH}. As development continues toward the nominal mask edge position, increasing values of m in the latent image give rise to lower development rates. Finally, as the desired dimension is approached, the development rate becomes very slow in what is nominally unexposed photoresist. For this to be true, the exposure at the mask edge must be such that m is greater than m_{TH}. One can see that the required exposure energy is a function of the value of m_{TH}.

Further defining the effects of development on the process, it can be shown that an optimum point of operation is to have the exposure at the mask edge be at the knee of the development rate curve (see Figure 4). This condition is a result of two competing requirements: process latitude is enhanced when the development rate at the mask edge is low, and greater selectivity between exposed and unexposed resist is obtained when the development rate at the mask edge is near the threshold point. By operating near the knee of the development rate curve a reasonable compromise is achieved.

Turning back to the problem at hand, what are the development properties which must be met in order to take advantage of the optimum latent image? For now we shall pick our latent image to have a PAC concentratio of 0.5 at the mask edge. From the above discussion, this means that m_{TH} must be less than 0.5. Further, if a value of $m=0.5$ is to be at the knee of the development rate curve, the threshold value must be in the range of approximately 0.2 to 0.3. This puts a very important restriction on the resist/developer system which can be used since many typical systems have values of m_{TH} of 0.6 to 0.8.

The three remaining development rate parameters can also be discussed. Obviously, it is desirable to have r_{min} as low as possible and to have the selectivity parameter n as large as possible. It is not obvious how r_{max} affects the development process from the point of view of linewidth control. To determine this, and the role of development time, a more rigorous analysis of development is needed.

Development Optimization

The development process can be characterized by two pieces of information: the development rate as a function of position within the resist r(x,z), and the physical development path, i.e., the position of the resist surface as a function of development time. The first property can be broken down into the development rate as a function of PAC concentration r(m), and the latent image m(x,z). Calculation of the latent image is straightforward and well understood. Models for r(m) exist[8], but much work needs to be done to further understand and characterize this function. The remainder of this section will deal with determining the path of development and how this knowledge can be used to optimize the development process.

The basic equation which defines the physical process of development is an integral equation of motion:

$$t_{dev} = \int_{(x_0,0)}^{(x,z)} \frac{ds}{r(x,z)} \qquad (14)$$

where t_{dev} is the development time, $(x_0,0)$ and (x,z) are the starting and ending points of the path, respectively, and ds is the differential path length. This integral is a line integral, meaning it is dependent on the path z(x). Thus, the integral cannot be solved unless the path is known.

One approach to solving equation (14) is to assume a particular path, preferably one with some physical validity. One reasonable assumption is that the path is segmented into vertical and horizontal components. Development proceeds vertically to some depth z, then horizontally to position x. Thus, equation (14) would become

$$t_{dev} = \int_{(x_0,0)}^{(x_0,z)} \frac{dz}{r(x,z)} + \int_{(x_0,z)}^{(x,z)} \frac{dx}{r(x,z)} \qquad (15)$$

Given a standard integral equation such as (15), many interesting and important results can be obtained. For example, the change in resist linewidth with exposure can be determined by differentiating equation (15) with respect to lnE, the logarithm of exposure energy, giving

$$\frac{\partial x}{\partial \ln E} = r(x,z)\gamma t_{dev} \qquad (16)$$

where γ is an average photoresist contrast as defined in Appendix A. Equations (15) and (16) have been derived previously and were used in the formulation of the Lumped Parameter model[4,5].

Much insight into the lithographic process can be gained from equation (16). Since the left-hand side of this equation represents the change in linewidth with exposure energy, this function should be minimized. Consider the development rate at the mask edge r(x,z). It can be made small, for example, by adjusting the exposure at the mask edge to be at the knee of the development rate curve. If the exposure at the mask edge is less than this amount, the development rate will be lower, but the development time will be higher to get the same final dimension. Thus, the knee represents the best point of operation. Also, there is reciprocity between development rate and development time. A photoresist with a high value of r_{max} requires a short development time, whereas a low r_{max} needs a longer development time.

The role of the contrast in equation (16) is less obvious. At first glance, one would expect that a higher contrast would result in worse exposure latitude. However, by examining Figure 5 one can see that increasing contrast (increasing n) causes a reduction of the development rate in the knee region. The overall effect is a decrease in the produce $r(x,z)\gamma$ and thus, an improvement in exposure latitude. If, however, the point of operation is not in the knee region, the exposure latitude may worsen with increasing contrast. As a final point, since the development rate is decidedly not linear with exposure energy, it is easy to conclude that there is not reciprocity between exposure energy and development time.

Although assuming a particular development path can greatly simplify the problem, it is not a necessary step in solving equation (14). The path can be determined exactly using the principle of least action[9]. In this case, least action means that the path of development will be such that the development time is a minimum. This restriction

completely defines the path for a given r(x,z) and can be defined by the Euler-Lagrange equation as shown below.

For a given funtion f(x,z,z´), the integral

$$\int_{x_A}^{x_B} f(x,z,z')dx \qquad (17)$$

is minimized when

$$\frac{\partial f}{\partial z} - \frac{d}{dx}\left(\frac{\partial f}{\partial z'}\right) = 0 . \qquad (18)$$

Expanding the total differential in the Euler-Lagrangian (equation 18)) gives

$$\frac{\partial f}{\partial z} - \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial z'}\right) - \frac{\partial}{\partial z}\left(\frac{\partial f}{\partial z'}\right)z' - \frac{\partial}{\partial z'}\left(\frac{\partial f}{\partial z'}\right)z'' = 0 . \qquad (19)$$

For our case, equation (14) can be put into the form of equation (17) as

$$t_{dev} = \int_{x_0}^{x} \frac{(1+z'^2)^{\frac{1}{2}}dx}{r(x,z)} \qquad (20)$$

so that

$$f(x,z,z') = \frac{(1+z'^2)^{\frac{1}{2}}}{r(x,z)} \qquad (21)$$

Substituting equation (21) into (19), the Euler-Lagrange equation becomes

$$z'' + [1+z'^2]\left(\frac{\partial \ln r}{\partial z} - z'\frac{\partial \ln r}{\partial x}\right) = 0 . \qquad (22)$$

A solution of equation (22) will give the development path z(x).

Let us first examine one simple case in which the development rate does not vary with depth into the resist. This corresponds to A=B=0 and exposure on a non-reflecting substrate. For this case, the resulting differential equation

$$z'' = [1+z'^2]\, z'\frac{\partial \ln r}{\partial x} \qquad (23)$$

can be integrated directly with the boundary condition that

$$z' \to \infty \quad at \quad z=0 .$$

This condition is equivalent to saying that the development path begins vertically. The result is

$$z' = \frac{r(x)}{[r^2(x_0)-r^2(x)]^{\frac{1}{2}}} . \qquad (24)$$

Thus, the development path is defined by

$$z = \int_{x_0}^{x} \frac{r(x)\,dx}{[r^2(x_0)-r^2(x)]^{\frac{1}{2}}} \qquad (25)$$

and equation (14) becomes

$$t_{dev} = \int_{x_0}^{x} \frac{r(x_0)}{r(x)} \frac{dx}{[r^2(x_0)-r^2(x)]^{\frac{1}{2}}} . \qquad (26)$$

Numerically carrying out the integrations in equations (25) and (26) results in a development path. By repeating the procedure for different starting points (x_0), a series of paths are generated which can be combined to give a resist profile. Figure 6 shows a typical case. The result compares very well with calculations performed with PROLITH[4], which makes the assumption that the development paths are perpendicular to the resist surface. For the more typical case of absorption and bleaching during exposure, the differential equation (22) must be solved numerically. More work must be done on the Euler-Lagrangian approach to development in order to fully reap the benefits of this important technique.

Sidewall Angle

Besides process latitude (and related linewidth control), a second criterion for lithographic quality is the shape of the photoresist feature. The shape is most easily characterized by the sidewall angle

of the resist profile. The fact that real photoresist profiles are not 90 degrees is due to two factors: absorption during exposure which causes sloped sidewalls of the latent image, and development with a finite contrast so that the top portions of the resist profile are under attack for a longer period of time than the bottom. Thus, in order to understand, and possibly optimize, the effects of the process on sidewall angle, one must look at both the exposure and development processes.

As previously discussed, exposure of the photoresist creates a latent image in the resist. Due to absorption, this latent image changes with depth into the resist. This change with depth can be determined by differentiating equation (5) with respect to z, obtaining

$$\frac{\partial m}{\partial z} = m[A(1-m) - B\ln(m)] \quad (27)$$

One can see that for no absorption (A=B=0) there will be no z-dependence of the latent image. Furthermore, when there is absorption the z-dependence is a function of exposure due to bleaching.

A sidewall slope of the latent image can be defined as the slope of a contour of constant PAC concentration. This corresponds to the resist sidewall slope for the limiting case of infinite developer selectivity. The latent sidewall slope can be determined by dividing $\partial m/\partial x$ by $\partial m/\partial z$ to obtain

$$latent\ slope = \frac{\ln(m_0)}{A(1-m_0) - B\ln(m_0)} \frac{\partial \ln(I_0)}{\partial x} \quad (28)$$

The latent sidewall angle is, of course, the inverse tangent of the slope. Note that the slope is directly proportional to the slope of the log-image, again pointing out the importance of this quantity.

Some insight into equation (28) can be gained by examining the cases of no exposure and complete exposure. In the limit of no exposure, the latent slope becomes a minimum:

$$latent\ slope = -\frac{1}{A+B} \frac{\partial \ln(I_0)}{\partial x} \quad (29)$$

In the limit of infiinite exposure, the slope becomes a maximum:

$$latent\ slope = -\frac{1}{B} \frac{\partial \ln(I_0)}{\partial x} \quad (30)$$

Between these two extremes, the slope increases monotonically with exposure. The results show that higher exposure energies result in better latent sidewall slopes. This effect is due to bleaching, where absorption decreases with increasing exposure.

The effects of development on sidewall angle are more difficult to define quantitatively. As can be seen from Figure 6, a resist with infinite latent sidewall slope (no absorption) will result in a finite resist sidewall slope due to the finite selectivity of the development process. As a first approximation, the final resist sidewall can be assumed to be perpendicular to the development path. Since, in the case of no absorption, the slope of the development path is given by equation (24), the resist slope becomes

$$resist\ slope \approx \left(\frac{r^2(x_0)}{r^2(x)} - 1\right)^{1/2} \quad (31)$$

For a good resist process, the development rate at x_0 (near the center of the space) will be much greater than that at the resist edge. Thus,

$$resist\ slope \approx \frac{r(x_0)}{r(x)} \quad (32)$$

From the point of view of development, the resist sidewall angle is optimized by increasing the ratio of $r(x_0)$ to $r(x)$.

Qualitatively, one can see how to maximize this ratio by examining Figure 4 or 5. Obviously, the exposure energy should be chosen so that $m(x_0) < m_{TH}$ and $m(x) > m_{TH}$. The choice of m(x) at the knee of the development rate curve qualitatively seems to be a good one since this allows r(x) to be small while letting $r(x_0)$ be as large as possible.

Conclusions

From the analysis given in this paper, several important conclusions can be drawn:

1) There is only one exposure energy which gives the optimum latent image: that which gives $m \approx 0.37$ at the mask edge. Thus, the practice of using exposure energy to compensate for process variations results in a process variation due to changing the latent image.

2) In practical terms, a nearly optimum latent image is obtained for a range of exposures which gives values of m of 0.2 to 0.5 at the mask edge. The exposure values in this range are two to three times greater than are typically used.

3) In order to take advantage of the optimum exposure range, the development process must be optimized. In particular, the threshold PAC concentration must be less than about 0.3.

4) In any resist system, optimum process latitude is obtained when exposure at the mask edge corresponds to a development rate at the knee of the development rate curve.

5) The Euler-Lagrange approach to development calculations provides an extremely useful tool for understanding and optimizing the development process.

Acknowledgements

The author wishes to thank Eytan Barouch for suggesting the Euler-Lagrange method as applied to development paths and for many stimulating discussions.

APPENDIX A

A Definition of Photoresist Contrast

The concept of contrast has long been used as a measure of the quality of an imaging system. As with any concept, however, its usefulness is limited by the rigorousness of its definition. When applied to the imaging properties of a photoresist, the concept of contrast has found some qualitative, but little quantitative, use due to the lack of a suitable definition. It is the intent of this appendix to propose a strict mathematical definition of photoresist contrast that embodies the concept and allows for quantitative use.

The term contrast is quite familiar to photolithography engineers. Qualitatively, it is a measure of the ability of a photoresist to reproduce an image. High values of photoresist contrast are associated with higher resolution, more vertical resist sidewalls, and better or worse process latitude depending on which lithography engineer is asked. The "definition" commonly associated with contrast involves a graph known as the *characteristic curve* of a photoresist. This curve plots the thickness of photoresist remaining after development as a function of the logarithm of the exposure energy. An example is shown in Figure A-1. Often a base-10 logarithm is used as the abscissa, but the natural log is preferred. Based on the characteristic curve, the contrast, given the symbol γ, is commonly "defined" as the negative of the slope of this curve as the thickness goes to zero.

$$\left.\frac{\partial T_r}{\partial \ln E}\right|_{T_r=0} = -\gamma. \qquad \text{(A-1)}$$

Problems immediately arise with this definition. First, the definition is not based on a theoretical examination of the contrast concept, but rather on an experimentally determined curve. As such, the value obtained is a function of experimental conditions. This problem is common enough in engineering. However, since there is no theoretical basis for the definition, it is impossible to determine which experimental conditions give a better measurement. Further, the definition of a quantity based on the method of measuring that quantity is not at all satisfactory. It is equivalent to

saying that a person's weight is defined as the number obtained when standing on a scale. Obviously, weight has a theoretically based definition, the force due to gravity, and the scale is just a method of measuring it. Similarly, for the contrast of a photoresist to be a useful term, it must have a theoretically based definition as well as experimental measurement methods.

In light of the above discussion, an alternate definition of photoresist contrast will be proposed and its relationship to the common definition will be given. Furthermore, some implications of this term as related to the concept of contrast will be given. Consider the following definition of contrast:

$$\gamma \equiv \frac{\partial lnR}{\partial lnE} \qquad \text{(A-2)}$$

where R is the development rate of the photoresist and is, of course, a function of energy. First, we shall consider this definition in relation to the characteristic curve. The thickness remaining after development can be obtained from the following,

$$T_r = 1 - \frac{1}{d}\int_0^t R\,dt \qquad \text{(A-3)}$$

where d is the initial photoresist thickness. Taking the derivative of this expression with respect to log-exposure energy yields

$$\frac{\partial T_r}{\partial lnE} = -\frac{1}{d}\int_0^t \frac{\partial lnR}{\partial lnE} R\,dt. \qquad \text{(A-4)}$$

Let us assume that the logarithmic derivative of development rate remains constant during the development so that this term can be removed from the integral. Therefore,

$$\frac{\partial T_r}{\partial lnE} = -\frac{\partial lnR}{\partial lnE}\left(\frac{1}{d}\int_0^t R\,dt\right) = -\frac{\partial lnR}{\partial lnE}(1-T_r). \qquad \text{(A-5)}$$

One can see that if this expression is evaluated at T_r=0, the term in parentheses becomes one and

$$\left.\frac{\partial T_r}{\partial lnE}\right|_{T_r=0} = -\frac{\partial lnR}{\partial lnE}. \qquad \text{(A-6)}$$

Thus the proposed definition of contrast given in equation (A-2) is equivalent to the common definition given the assumption that the contrast remains constant throughout the development time, or equivalently, over the thickness of the resist. To understand the validity of this assumption, and more importantly when this assumption is not valid, one must examine the properties of contrast as defined by equation (A-2).

Since development is a strong function of exposure energy, it is not at all obvious how the logarithmic derivative of development rate with respect to log exposure energy will behave. A typical development rate versus exposure energy dependence is plotted in Figure A-2 on a log-log scale. Thus, the slope of this curve is the contrast. As can be seen, there is a range of exposures where the contrast is relatively constant, and at its greatest value. At high and low exposures the contrast decreases, tending eventually to zero at the extremes of exposure.

Obviously, contrast is a function of exposure energy. When comparing the contrast measured with the characteristic curve to the theoretical definition, it was said that the two will agree if the contrast is constant over the thickness of the resist. This is equivalent to requiring that there be no variation in exposure energy as a function of depth into the photoresist. Alternately, if the exposure variations are within the linear portion of the curve of Figure A-2, the measurement will again produce the theoretical value of contrast. An example of when the characteristic curve measurement of contrast does not produce an accurate value is when the resist is heavily dyed. In this case the exposure energy will vary greatly with depth into the resist resulting in a measured value of contrast which is averaged over a range of energies. If this range is wide enough to extend into the low contrast regions of Figure A-2, the result will be a measured contrast which is lower than the theoretical value.

The theoretical definition of equation (A-2) can be used to quantify the concept of contrast as a measure of the quality of the photoresist imaging process. Based on this definition, it is easy to see that

$$\frac{\partial lnR}{\partial x} = \gamma\frac{\partial ln(I_o)}{\partial x}. \qquad \text{(A-7)}$$

The slope of the aerial image is related to the development rate gradient by the contrast. Further, one can think of contrast as amplifying the aerial image gradient to produce a development rate gradient. Higher values of contrast produce greater development rate gradients which, ultimately, give superior resist images. This is the basis of the contrast concept: the relationship between aerial image quality and photoresist image quality.

APPENDIX B

Applications to Contrast Enhancement Lithography

There are various techniques in photolithography which have been labeled *contrast enhancement lithography* (CEL). They include the most common, the CEL process developed by General Electric[10-12], as well as the Built-on-Mask (BOM)[13] and Photochemical Image Enhancement (PIE)[14] processes. They are all similar in that they involve the application of a separate photosensitive layer on top of the photoresist with the objective of creating a transmitted image through the top layer with superior contrast over the aerial image. In this appendix, the analysis given in this paper will be applied to these contrast enhancement techniques.

As with positive photoresists, the material used for contrast enhancement react upon exposure to light with first order kinetics. Thus, equations (1)-(6) can apply directly to exposure of a contrast enhancement material on a photoresist on a non-reflecting substrate. Of particular importance is the transmittance of the CEL film, which can be obtained from equation (6):

$$T = \frac{I}{I_0} = \frac{A(1-m) - B\,ln(m)}{A(1-m_0) - B\,ln(m_0)} \qquad \text{(B-1)}$$

where m_0 is the contrast enhancement material's PAC concentration at the top of the film and m is the concentration at the bottom of the film. Also, the gradient of PAC concentration is given by equation (10).

We will now simplify the problem by assuming that the non-bleachable absorption is negligible (i.e., B=0). This is a very good approximation for the commercially available GE materials. For this case, the PAC concentration is given by equation (13) and the transmittance becomes

$$T = \frac{(1-m)}{(1-m_0)} = \frac{m}{m_0}e^{-Ad} = \frac{1}{1+m_0(e^{Ad}-1)} = 1 + m(e^{-Ad}-1) \qquad \text{(B-2)}$$

where d is the contrast enhancement layer thickness. These basic equations will now be applied to the various CEL processes.

BOM and PIE

The BOM and PIE processes expose the enhancing material and the photoresist in separate exposure steps. First, the top PIE or BOM layer is exposed at a wavelength at which the photoresist is not sensitive. This top exposed layer is then fixed and the resist is flood exposed through the top layer. Thus, the image which exposes the photoresist is just the transmittance of the contrast enhancing layer, T(x). As we have seen, the resist PAC gradient and sidewall angle are proportional to the slope of the log-image. For a PIE or BOM system, the important quantity is thus $\partial lnT/\partial x$. From equation (B-2),

$$\frac{\partial lnT}{\partial x} = (1-e^{Ad})\,T(x)\,m_0\,ln(m_0)\,\frac{\partial lnI_0}{\partial x} \qquad \text{(B-3)}$$

The goal is to optimize the CEL transmitted image by maximizing the slope of the log-transmittance at the mask edge. Since this quantity is a function of exposure, what is the optimum exposure of the BOM or PIE layer to produce the best transmitted image?

This question is answered by differentiating equation (B-3) with respect to m_0 to determine the maximum. Designating the value of m_0^*, this value is given by the transcendental equation

$$m_0^* = \frac{1 + ln(m_0^*)}{(1-e^{Ad})} \qquad \text{(B-4)}$$

At this value, the transmittance becomes

$$T^* = -\frac{1}{ln(m_0^*)} \qquad \text{(B-5)}$$

and the slope of the log-transmittance is at its maximum

$$\left.\frac{\partial lnT}{\partial x}\right|_{max} = -\left(1-\frac{1}{T^*}\right)\frac{\partial lnI_0}{\partial x} \quad \text{(B-6)}$$

One can see from this equation that if T* is less than 0.5, the transmitted image will be better than the aerial image. But if T* is greater than 0.5, the transmitted image will be worse. Thus, this "break-even" value of T* will determine, from equations (B-4) and (B-5), a minimum value of Ad, the bleachable absorbance of the CEL film, for which contrast is enhanced. This value is

$$Ad_{min} = ln(e^2+1) \approx 2.13 \,. \quad \text{(B-7)}$$

Contrast is improved when Ad exceeds this value, but only at the optimum exposure. Thus, in practice the value of Ad must be significantly greater than this to effect the desired result.

One can define a *contrast enhancement factor* (CEF), which quantifies the improvement in the slope of the log-image, as

$$CEF = \frac{\partial lnT/\partial x}{\partial lnI_0/\partial x} \,. \quad \text{(B-8)}$$

Using the analysis given above, one can plot the CEF of a BOM or PIE process as a function of exposure for various values of bleachable absorbance (Figure B-1).

An implicit assumption in the above analysis is that the wavelengths of the flood exposure of the photoresist and the exposure of the enhancing material are the same. In fact, two different wavelengths are used with, most probably, different values of the absorbances. If the exposure of the PIE or BOM material results in a transmittance T_1 for a bleachable absorption coefficient A_1, and the second flood exposure has a concentration dependent absorption coefficient A_2 resulting in a transmittance T_2, all of the above equations apply to A_1 and T_1. The transmittance of importance, T_2, can be calculated from

$$T_2 = T_1^{A_2/A_1} \quad \text{(B-9)}$$

and

$$\frac{\partial lnT_2}{\partial x} = \frac{A_2}{A_1}\frac{\partial lnT_1}{\partial x} \quad \text{(B-10)}$$

Thus, the results above apply with the factor A_2/A_1 included. If A_2 is greater than A_1, the results are improved. If A_2 is less than A_1, the results are worsened.

Standard CEL

The standard contrast enhancement process, as developed by General Electric, exposes the enhancing material and the photoresist at the same time. Thus, the image reaching the photoresist I_T is the produce of the aerial image and the transmittance of the CEL film.

$$I_T = T(x)\,I_0(x) \,. \quad \text{(B-11)}$$

Since T(x) is a function of exposure, the transmitted image changes with exposure time. Thus, the defining equations for exposure apply to the CEL material, but do not apply to the exposure of the photoresist. As a simple approach, however, one can ignore bleaching in the photoresist so that the exposure energy within the resist will be

$$E = \int_0^t I_T(x)\,dt = I_0(x)\int_0^t T(x)\,dt \quad \text{(B-12)}$$

and the PAC concentration just

$$m' = exp\left(-C'E\right) = exp\left(-C'\int_0^t I_T(x)\,dt\right) \quad \text{(B-13)}$$

where the primes are used to designate the photoresist properties. Using equation (B-2) for the transmittance of the CEL film, the integral of transmittance over exposure time can be evaluated analytically using

$$m_0 = exp\left(-CI_0t\right). \quad \text{(B-14)}$$

The result is

$$\int_0^t T(x)\,dt = t - \frac{1}{CI_0} ln\left(\frac{T_f}{T_i}\right) = t\left(1 + \frac{ln(T_f/T_i)}{ln(m_o)}\right) = t\,\frac{ln(m)}{ln(m_o)} \qquad \text{(B-15)}$$

where T_i and T_f represent the initial and final transmittances of the CEL film, respectively. The initial transmittance is not a function of x and is given by

$$T_i = e^{-Ad} \qquad \text{(B-16)}$$

Substituting equation (B-15) into (B-13) gives

$$m' = exp\left(-C' I_0(x)t\right) exp\left(\frac{C'}{C} ln[T_f/T_i]\right) = \left(\frac{m_0 T_f}{T_i}\right)^{C'/C} \qquad \text{(B-17)}$$

One can now use equation (B-17) to determine, and subsequently optimize, the photoresist PAC gradient. By differentiating equation (B-17) with respect to x,

$$\frac{\partial m'}{\partial x} = a\, m' T_f\, ln(m_0) \frac{\partial ln(I_0)}{\partial x} \qquad \text{(B-18)}$$

where α is the ratio of the resist to CEL exposure rate constants, C'/C. From this equation, it is possible to optimize the exposure to achieve a maximum PAC gradient. This optimum exposure occurs when the following transcendental equation is satisfied:

$$[(a+1)T_f - 1]\, ln(m_0) + 1 = 0\,. \qquad \text{(B-19)}$$

One can further optimize the PAC gradient in the photoresist by finding the value of α which gives the best gradient. By differentiating equation (B-18) with respect to α and setting the result equal to zero, the optimum value of α occurs when m' takes a value of 0.37. Thus, these two restrictions for maximum PAC gradient give a specific value to α as a function of the CEL bleachable absorbance Ad. This best value is shown in Figure B-2.

It is interesting to compare the theoretically optimal CEL conditions to typical values using the commercially available CEM-388. This material exposes about three to four times faster than standard photoresist so that α is about 0.25[15]. For a typical application, the CEM-388 thickness is about 0.4 µm and the value of A is about 12 μm^{-1}, making Ad equal to about 5. From Figure B-2, it is obvious that this value of α is not close to the optimum value. For CEM-388, equation (B-19) gives the best exposure as that which gives a PAC concentration in the photoresist of 0.55 at the mask edge.

As in the BOM and PIE case, a contrast enhancement factor can be defined as the ratio of the PAC gradients with and without CEL for a given exposure level (i.e., a given value of m'). Using equation (B-18) for the CEL case and equation (11) for the resist alone,

$$CEF = a\, T_f \frac{ln(m_0)}{ln(m')} = T_f \frac{ln(m_0)}{ln(m)} \qquad \text{(B-20)}$$

One can define an average transmittance of the CEL film over the course of the exposure as

$$T_{AVG} = \frac{1}{t}\int_0^t T(x)\,dt\,. \qquad \text{(B-21)}$$

By examining equation (B-15), one can see that the CEF can also be written as

$$CEF = \frac{T_f}{T_{AVG}} \qquad \text{(B-22)}$$

Since the final transmittance will always be greater than the average transmittance, the CEF will always be greater than one. A plot of the contrast enhancement factor as a function of CEL absorbance is given in Figure B-3 for different values of α. In all cases, the optimum exposure is used. As can be seen, α equal to 1, corresponding to equal exposure rates for the photoresist and the CEL, seems to be a fairly good compromise over a wide range of Ad values.

Again looking at CEM-388 as a typical process, the PAC gradient is enhanced by a factor of about 2.5 for an Ad of 5 when the exposure is optimized. This results in significant improvement in process latitude. The effects of contrast

enhancement lithography on exposure latitude and development latitude, though not shown here, can be investigated using the techniques described in this paper along with the equations derived in this appendix.

REFERENCES

1. J. Albers and D. B. Novotny, "Intensity Dependence of Photochemical Reaction Rates for Photoresists," Ô. Electrochem. Soc., Vol. 127, No. 6, pp. 1400-1403 (June, 1980).

2. F. H. Dill, et al., "Characterization of Positive Photoresist," IEEE Trans. Electron Dev., ED-22, No. 7, pp. 445-452 (1975) and Kodak Microelec. Sem Interface '74, pp. 44-54 (1974).

3. S. V. Babu and E. Barouch, "Exact Solution of Dill's Model Equations for Positive Photoresist Kinetics," IEEE Electron Device Lett., Vol. EDL-7, No. 4, pp. 252-253 (April, 1986).

4. R. Hershel and C. A. Mack, "Lumped Parameter Model for Optical Lithography," Chapter 2, Lithography for VLSI, VLSI Electronics - Microstructure Science, R. K. Watts and N. G. Einspruch, eds., Academic Press, pp. 19-55 (New York:1987).

5. C. A. Mack, A. Stephanakis, R. Hershel, "Lumped Parameter Model of the Photolithographic Process," Kodak Microelec. Seminar Interface '86, pp. 228-238 (1986).

6. C. A. Mack, "PROLITH: A Comprehensive Optical Lithography Model," Optical Microlith. IV, Proce., SPIE Vol. 538, pp. 207-220 (1985).

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

8. C. A. Mack, "Development of Positive Photoresist," J. Electrochem. Soc., Vol. 134, No. 1, pp. 148-152 (January 1987).

9. E. Barouch, work in progress

10. B. F. Griffing and P. R. West, "Contrast Enhanced Photolithography," IEEE Elect. Dev. Let., Vol. EDL-4, No. 1, pp. 14-16 (January 1983).

11. P. R. West and B. F. Griffing, "Contrast Enhanced - a Route to Submicron Optical Lithography," Optical Microlith. II, Proc., SPIE Vol. 394, pp. 33-38 (!983).

12. B. F. Griffing and P. R. West, "Contrast Enhanced Photoresists - Processing and Modeling," Polymer Eng. Sci., Vol. 23, No. 17, pp. 947-952 (December 1983).

13. F. A. Vollenbroek, et. al., "High Resolution Optical Lithography by Formation of a Built On Mask (BOM)," Microel. Eng., Vol. 3, Nos. 1-4, pp. 245-252 (December 1985).

14. J. R. Sheats, M. M. O'Toole, and J. S. Hargreaves, "Photochemical Image Enhancement (PIE)," Adv. Resist Tech. III, Proc., SPIE Vol. 631, pp. 171-177 (1986).

15. C. A. Mack, "Contrast Enhancement Techniques for Submicron Optical Lithography," J. Vac. Sci. Tech., Vol. A5, No. 4, pp. 1428-1431 (July/August 1987).

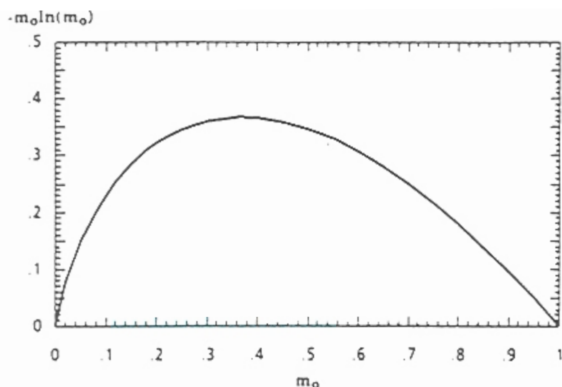


Figure 1. Variation of latent image slope with PAC concentration m_o.

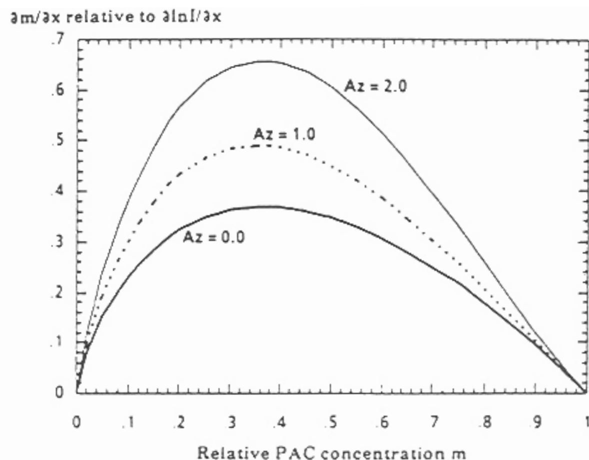


Figure 2. Variation of latent image slope with PAC concentration m when B = O.

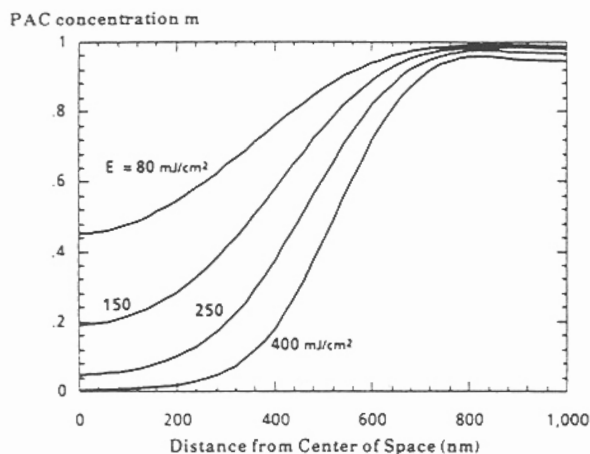


Figure 3. PAC latent images for different exposure energies (Az = 0.6, Bz = 0.05, C = $0.04 cm^2/mj$).

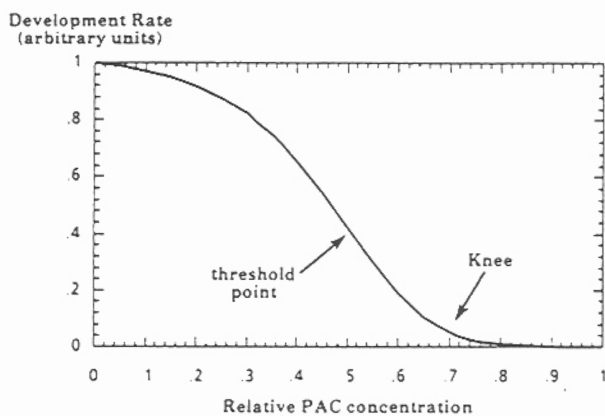


Figure 4. Typical development rate curve.

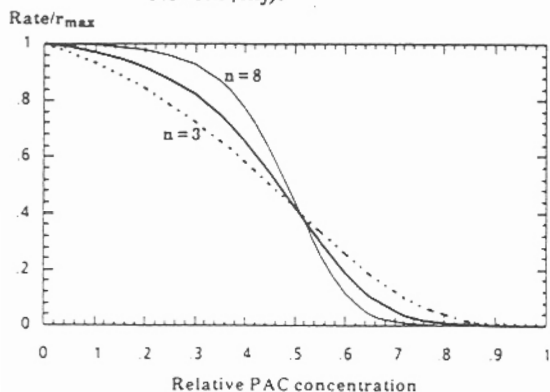


Figure 5. Kinetic development rate model for n = 3, 5, and 8 ($m_{th} = 0.5$, $r_{min} = 0$)

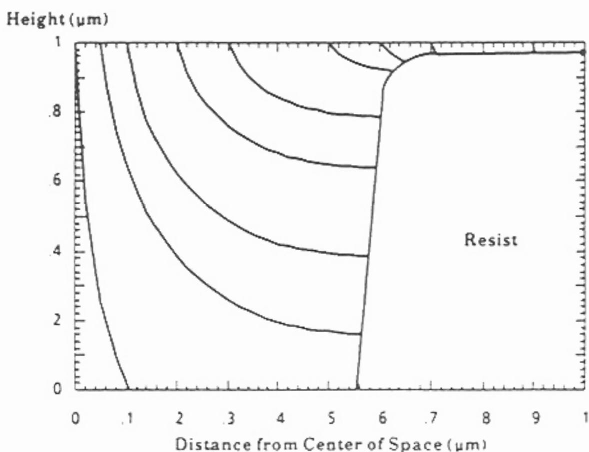


Figure 6. Development paths based on Euler-Lagrange analysis (A = B = 0).

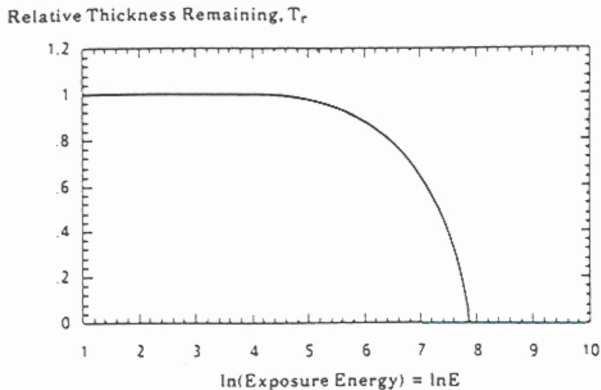


Figure A-1. Characteristic curve of a positive photoresist.

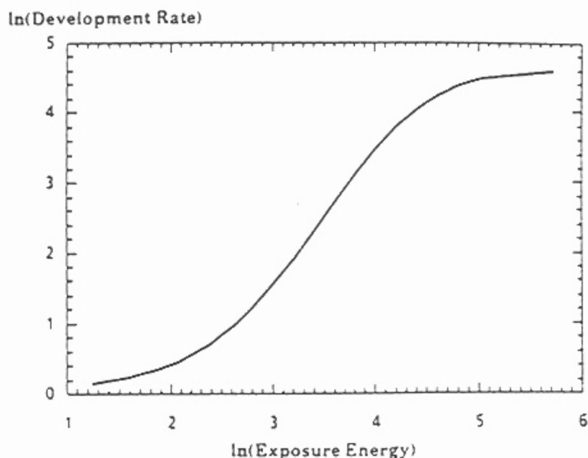


Figure A-2. Theoretical definition of constrast is the slope of this curve.

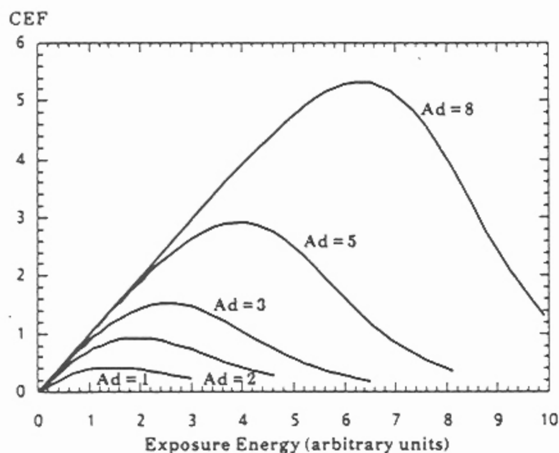


Figure B-1. Constrast Enhancement Factor (CEF) of the BOM and PIE processes as a function of exposure for different material absorbances.

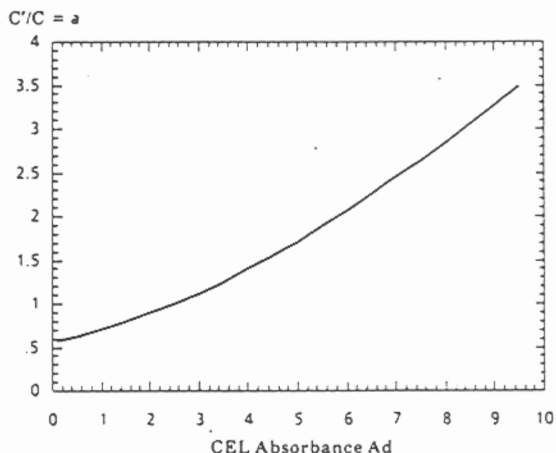


Figure B-2. Optimum value of the relative resist exposure rate as a function of CEL absorbance.

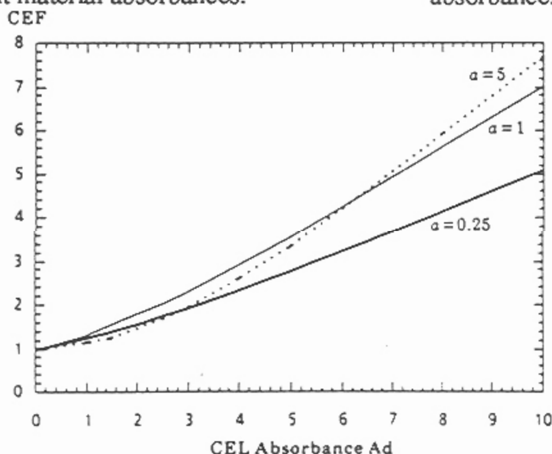
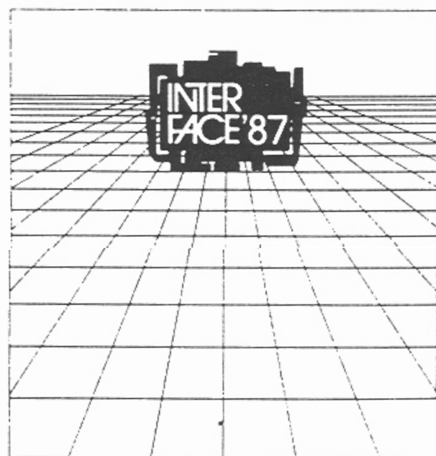


Figure B-3. Contrast Enhancement Factor of the standard CEL process for different relative exposure rates *a* (at the optimum exposure).

KTI CHEMICALS INCORPORATED

$15.95



KTI MICROELECTRONICS SEMINAR

PROCEEDINGS

Sponsored by KTI Chemicals, Inc.
November 19-20, 1987
San Diego, California