

# Diffusion and Resolution for Chemically Amplified Resists

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As discussed in the last edition of this column (*MLW*, May 2006), diffusion in conventional (non-chemically amplified) resists has a very predictable (and undesirable) impact on resolution. The effects of diffusion can be determined by convolving the pre-diffusion latent image with a diffusion “point spread function”, which for Fickean (constant diffusivity) diffusion is simply a Gaussian whose sigma is equal to the diffusion length.

$$m^*(x) = m(x) \otimes DPSF = \frac{1}{\sqrt{2\pi}\sigma_D} \int_{-\infty}^{\infty} m(\tau) e^{-(x-\tau)^2/2\sigma_D^2} d\tau \quad (1)$$

where  $m(x)$  is the (1D) latent image after exposure,  $m^*(x)$  is the latent image after diffusion, and  $\sigma_D$  is the diffusion length. This diffusion point spread function (*DPSF*) is the final chemical distribution after a bake if the initial concentration profile had been an ideal delta-function of concentration.

For chemically amplified resists, things are a bit more complicated. Diffusion during post-exposure bake is accompanied by a deblocking reaction that changes the solubility of the resist. Thus, it is not the final, post-diffusion distribution of exposure reaction products that controls development but rather the integral over time of these exposure products. Things become even more complicated when acid loss is accounted for. In particular, the presence of base quencher (that also may diffuse) leads to both complexity and advantage in tailoring the final latent image shape. However, for the simplified case of no acid loss, an analytical solution is possible.

Letting  $h(x, t = 0)$  be the concentration of acid (the exposure product) at the beginning of the post-exposure bake (PEB), an effective acid latent image can be defined as

$$h^*(x) = \frac{1}{t_{PEB}} \int_0^{t_{PEB}} h(x, t = 0) \otimes DPSF dt = h(x, 0) \otimes \frac{1}{t_{PEB}} \int_0^{t_{PEB}} DPSF dt = h(x, 0) \otimes RDPSF \quad (2)$$

where *RDPSF* is the reaction-diffusion point spread function [1]. This effective acid concentration distribution  $h^*(x)$  can be used to calculate the reaction kinetics of the PEB as if no diffusion had taken place. In other words, the effects of diffusion is separable from the reaction for the case of no acid loss. The *RDPSF* then becomes analogous to the *DPSF* of a conventional resist.

For the 1D case (which will be useful for our subsequent discussion of resolution), the Gaussian diffusion kernel is affected by time integration through the diffusion length,  $\sigma_D = \sqrt{2Dt}$ , where  $D$  is the acid diffusivity in resist. Thus,

$$RDPSF = \frac{1}{t_{PEB} \sqrt{4\pi D}} \int_0^{t_{PEB}} \frac{e^{-x^2/4Dt}}{\sqrt{t}} dt \quad (3)$$

The integral is solvable, resulting in an interesting final solution.

$$RDPSF(x) = 2 \frac{e^{-x^2/2\sigma_D^2}}{\sqrt{2\pi}\sigma_D} - \frac{|x|}{\sigma_D^2} erfc\left(\frac{|x|}{\sqrt{2}\sigma_D}\right) \quad (4)$$

The first term on the right hand side of equation (4) is nothing more than twice the *DPSF*, and thus accounts for pure diffusion. The second term, the complimentary error function times  $x$ , is a reaction term that is subtracted and thus reduces the impact of pure diffusion. Each term, as well as the final *RDPSF*, is plotted in Figure 1.

One of the most important properties of the *RDPSF* is that it falls off in  $x$  much faster than the *DPSF* with the same diffusion length. The full width half maximum for the *DPSF* is about  $2.35\sigma_D$ , but for the *RDPSF* it is about  $\sigma_D$ . Also, invoking a large argument approximation for the *Erfc*,

$$\frac{RDPSF(x)}{DPSF(x)} \approx \left( \frac{2\sigma_D^2}{x^2} \right), \quad x \gg \sigma_D \quad (5)$$

In other words, a reaction-diffusion resist system can tolerate more diffusion than a conventional resist system.

To further compare reaction-diffusion to pure diffusion, consider again the impact of diffusion (and reaction-diffusion) on resolution. As in the last column, we'll use a generic latent image for a repeating line/space pattern of pitch  $p$  described as a Fourier series:

$$h(x,0) = \sum_{n=0}^N a_n \cos(2\pi nx/p) \quad (7)$$

where a pattern symmetrical about  $x = 0$  is assumed so that there are no sine terms in the series. Larger values of  $n$  represent higher frequency terms (harmonics) in the image, though a typical high resolution dense pattern will have an upper limit of  $N = 2$  or  $3$ . The effect of pure diffusion, calculated as a convolution with the *DPSF*, is simply a reduction in the amplitude of each harmonic.

$$h^*(x) = \sum_{n=0}^N a_n^* \cos(2\pi nx/p) \quad (8)$$

where

$$a_n^* = a_n e^{-2(\pi n \sigma_D / p)^2}$$

In the reaction-diffusion case, we convolve equation (7) with the *RDPSF*, which results in an analytical solution [2]:

$$a_n^* = a_n \left( \frac{1 - e^{-2(\pi n \sigma_D / p)^2}}{2(\pi n \sigma_D / p)^2} \right) \quad (9)$$

Figure 2 compares the effects of pure diffusion with reaction-diffusion on the amplitudes of the Fourier coefficients. As can be seen, pure diffusion causes a much faster degradation of the Fourier components than reaction-diffusion. For example, if one is willing to allow a particular Fourier component to fall in amplitude by 20%, a reaction-diffusion system with no acid loss can tolerate about 50% more diffusion than a pure diffusion resist.

The above analysis is very helpful for understanding the role of diffusion in a simple reaction-diffusion system with no acid loss. However, all serious chemically amplified resists include base quenchers – a beneficial source of acid loss. For one special case the above analysis applies even when quencher is present. If the acid-quencher reaction is very fast compared to diffusion (a very good assumption), and the base quencher has exactly the same diffusivity as the acid, then the initial acid concentration at the start of the PEB  $h(x,0)$  is simply reduced by the background quencher concentration. (Note that for a Fourier series representation of the initial acid latent image such as equation (8), the impact of quencher is then just a reduction of the value of  $a_0$ .) Negative acid concentrations represent base quencher and both acid and base diffusion are properly calculated using the convolution of equation (2). Of course, negative values of  $h^*(x)$ , the effective acid concentration, should be set to zero before performing any amplification calculations.

## References

1. J. D. Byers, M. D. Smith, and C. A. Mack, “Lumped Parameter Model for Chemically Amplified Resists,” *Optical Microlithography XVII, Proc.*, SPIE Vol. 5377 (2004) pp. 1462-1474.
2. T. Graves, M. D. Smith, C. A. Mack, “Methods for Benchmarking Photolithography Simulators: Part IV,” *Optical Microlithography XIX, Proc.*, SPIE Vol. 6154 (2006).

## List of Figures

Figure 1. A plot of the 1D reaction-diffusion point spread function (RDPSF), labeled as Total in the graph, as well as the two components that make up this function. Both axes are scaled using the diffusion length,  $\sigma_D$ .

Figure 2. Effect of diffusion on the latent image frequency components for a dense line, comparing pure diffusion (DPSF) to reaction diffusion (RDPSF).

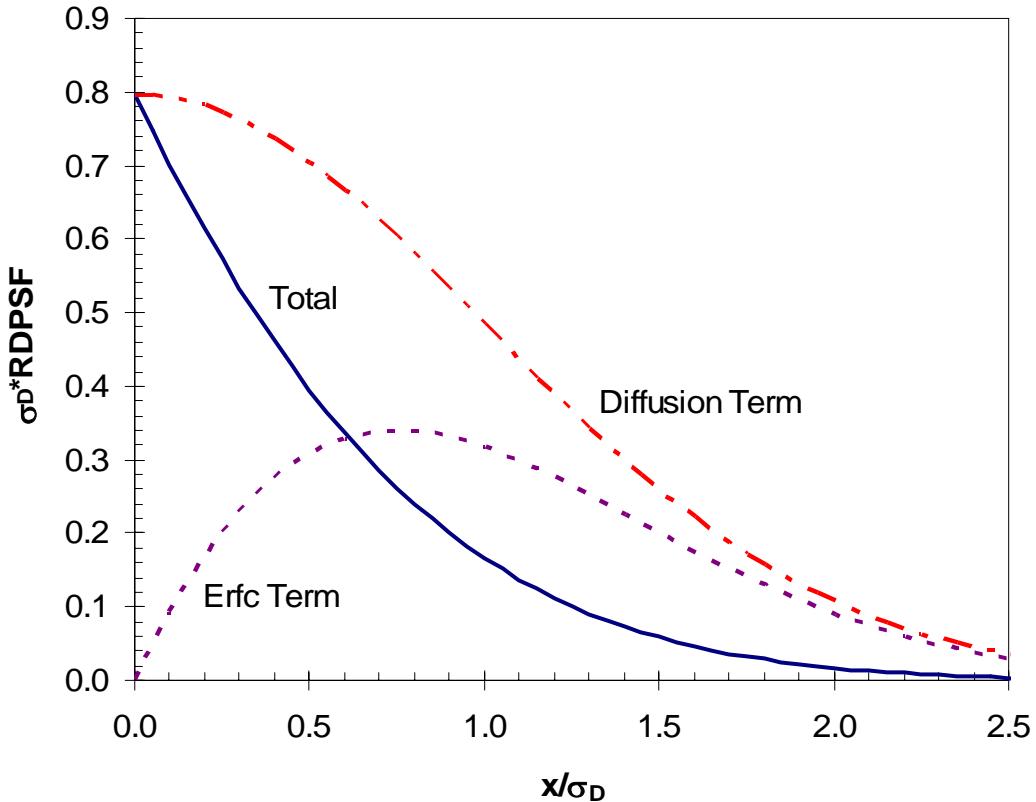


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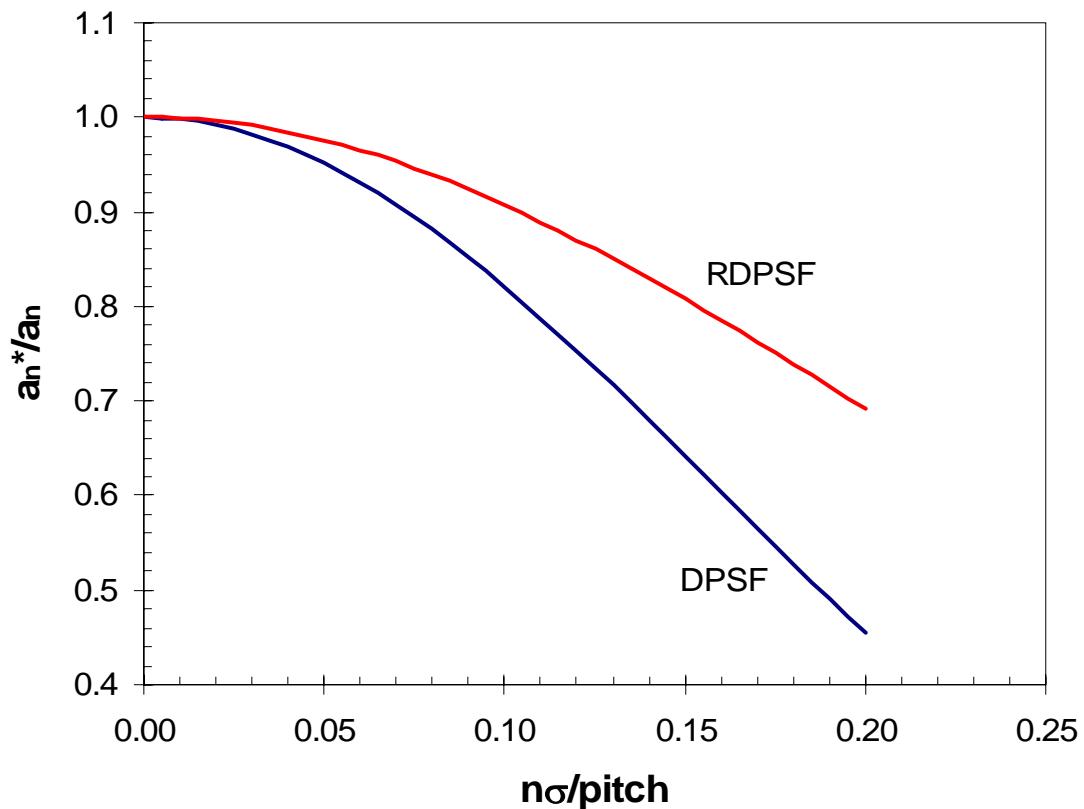


Figure 2. Effect of diffusion on the latent image frequency components for a dense line, comparing pure diffusion (DPSF) to reaction diffusion (RDPSF).