The Lithography Expert *(February 2007)*

Line Edge Roughness, part 1

While resolution is commonly discussed relative to optical limits, and sometimes even resist contrast limitations, it is quite possible that the ultimate limit of resolution will come from line edge roughness. When variations in the width of a resist feature occur quickly over the length of the feature, this variation is called *linewidth roughness* (see Figure 1). When examining these variations along just one edge it is called *line edge roughness* (LER). LER becomes important for feature sizes on the order of 100 nm or less, and can become the most significant source of linewidth control problems for features below 50 nm. LER is caused by a number of statistically fluctuating effects at these small dimensions such as shot noise (photon flux variations), statistical distributions of chemical species in the resist (such as photoacid generators), the random walk nature of acid diffusion during chemical amplification, and the non-zero size of resist polymers being dissolved during development.

It is important to note that most theoretical descriptions of lithography make an extremely fundamental (and mostly unstated) assumption about the physical world: the so-called *continuum approximation*. Even though light energy is quantized into photons and chemical concentrations are quantized into spatially distributed molecules, the descriptions of aerial images, latent images, and resist development rates usually ignore the discrete nature of these fundamental units and use instead continuous mathematical functions. A continuum mathematical model predicting the shape of the acid latent image after exposure is fundamentally incapable of predicting how statistical variations in photon and molecule numbers might contribute to LER. Thus, when describing lithographic behavior at the nanometer level, an alternate approach, and in a very real sense a more fundamental approach, is to build the quantization of light as photons and matter as atoms and molecules directly into the models used. Such an approach is called *stochastic modeling*, and involves the use of random variables and probability density functions to describe the situation. Such a probabilistic description, however, cannot state what will happen with certainty, but only give probabilities that depend on circumstances. In the first part of this series on LER, I'll tackle exposure and derive the statistics of the resulting acid concentration.

Photon Shot Noise

To begin, consider a light source that randomly emits photons at an average rate of L photons per unit time into some area A. Assume further that each emission event is independent. Over some small time interval dt (smaller than $1/L$ and small enough so that it is essentially impossible for two photons to be emitted during that interval), either a photon is emitted or it is not (a binary proposition). The probability that a photon will be emitted during this interval will be Ldt. Consider now some long time $T = Ndt$ ($\gg dt$). What can we expect for the number of photons emitted during the period T? This basic problem is called a Bernoulli trial and the resulting probability distribution is the well-known *binomial distribution*. If $NLdt = TL$ remains

finite as N goes to infinity, the binomial distribution converges to a more manageable equation for the probability of finding (n) photons called the Poisson distribution:

$$P(n) = \frac{(TL)^n}{n!} e^{-TL} \tag{1}$$

The Poisson distribution can be used to derive the statistical properties of photon emission. The expectation value of n (that is, the mean number of photons that will be emitted in a time interval T) is TL (a very reasonable result since L was defined as the average rate of photon emission). The variance (the standard deviation squared) is also TL. Note that the Poisson distribution differs from the familiar normal (or Gaussian) probability distribution; there is only one free parameter – the average, TL.

To use these statistical properties, we must convert from number of photons to a more useful measure, intensity. If n photons cross an area A over a time interval T, the intensity of light will be

$$I = \frac{n}{TA}\left(\frac{hc}{\lambda}\right). \tag{2}$$

The standard deviation of the intensity can then be computed from the properties of the Poisson distribution.

$$\frac{\sigma_I}{\langle I \rangle} = \frac{\sigma_n}{\langle n \rangle} = \frac{1}{\sqrt{\langle n \rangle}} = \left[\langle I \rangle TA\left(\frac{\lambda}{hc}\right)\right]^{-1/2} \tag{3}$$

As this equation shows, the fractional uncertainty of the intensity grows as the mean number of photons ($\langle n \rangle \propto \langle I \rangle TA$) is reduced, a phenomenon known as *shot noise*. The shot noise (the relative uncertainty in the actual intensity that the resist will see) increases with decreasing intensity, exposure time, and area of concern.

As an example, consider a 193 nm exposure of a resist with a dose-to-clear of 10 mJ/cm^2. At the resist edge, the mean exposure energy (= $\langle I \rangle T$) will be on the order of the dose-to-clear. At this wavelength, the energy of one photon, hc/λ, is about 1.03 X 10^{-18} J. For an area of 1 nm X 1 nm, the mean number of photons during the exposure, from equation (2), is about 97. The standard deviation is about 10, or about 10% of the average. For an area of 10 nm square, the number of photons increases by a factor of 100, and the relative standard deviation decreases by a factor of 10, to about 1%. Since these are typical values for a 193 nm lithography process, we can see that shot noise contributes a noticeable amount of uncertainty as to the actual dose seen by the photoresist when looking at length scales less than about 10 nm.

For Extreme Ultraviolet (EUV) lithography, the situation will be considerably worse. At a wavelength of 13 nm, the energy of one photon will be 1.53 X 10^{-17} J, more than fifteen times greater than at 193 nm. Also, the goal for resist sensitivity will be to have EUV resists that are 2 – 4 times more sensitive than 193 nm resists (though it is unclear whether this goal will be

achieved). Thus, the number of photons will be 30 – 60 times less for EUV than 193 nm lithography. A 1 nm X 1 nm area will see only 2 – 3 photons, and a 10 nm square area will see on the order of 200 photons, with a standard deviation of 7%.

Chemical Concentration

Interestingly, chemical concentration exhibits an uncertainty not unlike the incidence of photons. As mentioned above, there really is no such thing as concentration at a point in space since the chemical species is formed by discrete molecules, not a continuous medium. Concentration, the average number of molecules per unit volume, exhibits counting statistics identical to photon emission. Let C be the average number of molecules per unit volume, and dV a volume small enough so that at most one molecule may be found in it. The probability of finding a molecule in that volume is just CdV. For some larger volume V, the probability of finding exactly n molecules in that volume will be given by a binomial distribution exactly equivalent to that for photon counting. And, for any reasonably large volume ($CV > 1$), this binomial distribution will also be well approximated by a Poisson distribution. The average number of molecules in the volume will be CV, and the variance will also be CV. The relative uncertainty in the number of molecules in a certain volume will be, like for our photon statistics, equal to one over the square root of the number of molecules in that volume of interest.

As an example, consider a 193nm resist that has an initial PAG concentration of 3% by weight, or a concentration of about 0.07 mole/liter (corresponding to a density of 1.2 g/ml and a PAG molecular weight of 500 g/mole). Converting from moles to molecules with Avogadro's number, this corresponds to 0.042 molecules of PAG per cubic nanometer. In a volume of 10 nm cubed, the mean number of PAG molecules will be 42. The standard deviation will be 6.5 molecules, or about 15%. For 248 nm resists, the PAG loading is typically 3 times higher or more, so that closer to 150 PAG molecules might be found in a 10 nm cubed volume, for a standard deviation of 8%.

Photon Absorption and Exposure of One PAG Molecule

What is the probability that a photon will be absorbed by a molecule of light sensitive material in the resist? Further, what is the probability that a molecule of sensitizer will react to form an acid? As discussed above, there will be a statistical uncertainty in the number of photons in a given region of resist, a statistical uncertainty in the number of PAG molecules, and additionally a new statistical uncertainty in the absorption and exposure event itself.

Consider a single molecule of PAG. First order kinetics of exposure can be used to derive the concentration of PAG remaining after exposure (and, as well, the concentration of acid generated) in the continuum approximation. From a stochastic modeling perspective, this kinetic result represents a probability density function for reaction. Let y be a random variable that represents whether a given single PAG molecule was converted to acid or remains unexposed by the end of the exposure process (this is a binary proposition – either the PAG molecule reacts or it doesn't). Thus $y = 1$ means an acid has been generated (PAG has reacted), and $y = 0$ means the PAG has not generated acid (either it was not been exposed or reacted differently). A kinetic analysis of exposure gives us the probability for each of these states, given a certain intensity in the resist I:

$$P(y=0\,|\,I)=e^{-CIt}\,,\qquad P(y=1\,|\,I)=1-e^{-CIt} \tag{4}$$

where C is the exposure rate constant and t is the exposure time. For a given intensity, the mean value and variance of y can be calculated using the definition of a discrete probability expectation value. However, we know from our discussion of photon counting statistics that I is a probabilistic function. Thus, the mean and variance of y must take into account this probabilistic nature. Letting n be the number of photons exposing a given area A over an exposure time t, it will be useful to define a new constant in terms of photon number n:

$$CIt=\psi n \quad \text{which leads to} \quad \psi=\left(\frac{hc}{\lambda}\right)\frac{C}{A}=\frac{\Phi\sigma_{M-abs}}{A} \tag{5}$$

The term ψ is the *exposure shot noise coefficient*, and is equal to the acid generation quantum efficiency (Φ) multiplied by the ratio of the PAG absorption cross-section (σ_{M-abs}) to the area of statistical interest. Since the quantum efficiency is typically in the 0.3 – 0.7 range and the PAG absorption cross-section is on the order of 1 $Å^2$ for 193 nm resists, for most areas of interest this exposure shot noise coefficient will be much less than 1. For EUV resists, the PAG absorption cross-section is expected to be a bit larger, on the order of 30 $Å^2$.

Using this exposure shot noise coefficient to convert intensity to number of photons and then employing the properties of the Poisson distribution, the average probability of generating acid becomes:

$$\langle y\rangle = 1-e^{-\langle n\rangle\left(1-e^{-\psi}\right)} \tag{6}$$

As often happens when taking statistical distributions into account, the mean value of the output of the function is not equal to the function evaluated at the mean value of the input. The mean value of y is always less than the value of the function y evaluated at the mean value of the intensity, though the difference becomes small for $\psi \ll 1$. The impact of photon shot noise on the variance of the acid generation probability (y) can be calculated, giving

$$\sigma_y^2=\langle y\rangle-\langle y\rangle^2=\langle y\rangle\left(1-\langle y\rangle\right) \tag{7}$$

(This result is always true for a binary variable, being a fundamental result for any binomial distribution).

PAG Concentration After Exposure

The mean value and uncertainty of the state of *one* acid molecule after exposure can now be translated into a mean and uncertainty of the overall acid concentration after exposure. Consider a volume V that initially contains some number n_0 of PAG molecules. After exposure, the number of photogenerated acid molecules Y will be

$$Y = \sum_{i=1}^{n_0} y_i \tag{8}$$

where y_i is the discrete random variable representing the exposure state of the ith molecule found in this volume (all of which are assumed to be independent). For a given n_0, the mean and variance of Y can be readily computed. But n_0 itself has a Poisson statistical distribution, as discussed above. The mean value of Y including the statistical variation of n_0, is

$$\langle Y \rangle = \langle n_0 \rangle \langle y \rangle \tag{9}$$

Likewise, the variance of Y can be computed to give [2]

$$\sigma_Y^2 = \langle y \rangle^2 \sigma_{n_0}^2 + \langle n_0 \rangle \sigma_y^2 \tag{10}$$

Using equation (7) and relating the number of acid molecules per unit volume Y to the concentration of acid H,

$$\frac{\sigma_Y}{\langle Y \rangle} = \frac{\sigma_H}{\langle H \rangle} = \frac{1}{\sqrt{\langle Y \rangle}} = \frac{1}{\sqrt{\langle n_0 \rangle \langle y \rangle}} \tag{11}$$

The final result, which accounts for photon fluctuations, uncertainty in the initial concentration of photoacid generator, and the probabilistic variations in the exposure reaction itself, is reasonably intuitive. The relative uncertainty in the resulting acid concentration after exposure is equal to one over the square root of the mean number of acid molecules generated within the volume of interest. For large volumes and reasonably large exposure doses, the number of acid molecules generated is large and the statistical uncertainty in the acid concentration becomes small. For small volumes or low doses, a small number of photogenerated acid molecules results in a large uncertainty in the actual number within that volume. For the case of the 10 nm cube of 193 nm resist above, the 1 σ uncertainty in initial acid concentration near the resist edge will be >20%!

In the next edition of this column, we'll look at how this uncertainty in acid concentration propagates to an uncertainty in the concentration of blocked polymer after the reaction-diffusion of the post-exposure bake. The addition of development will complete the story, allowing us to predict the statistics of LER.

References

1. Chris A. Mack, Field Guide to Optical Lithography, SPIE Field Guide Series Vol. FG06, (Bellingham, WA: 2006).

2. The derivation of this result is quite messy, so I leave the mathematics to my forthcoming lithography textbook.

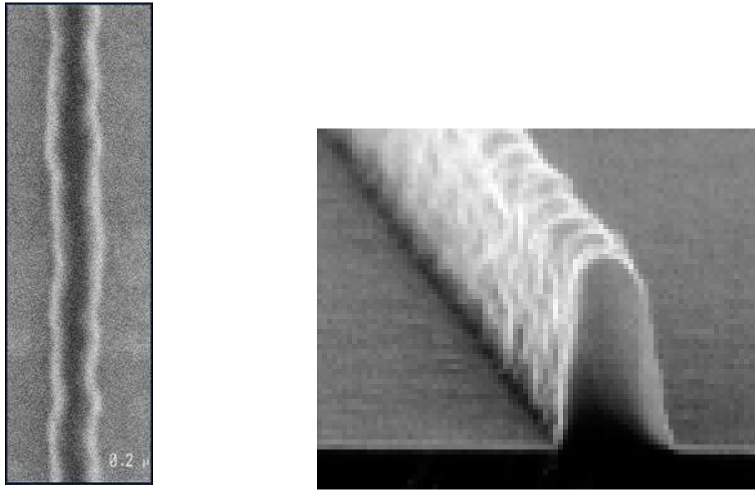

Figure 1 SEM pictures of photoresist features exhibiting line edge roughness (from Ref. 1).