Photoresist Development, part 1

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Development is an extremely critical step in the processing of photoresist. It is the development properties of a photoresist which dominate its performance. A "good" photoresist, one with good resolving properties, is a resist with "good" development properties. However, characterizing the development properties of a photoresist is not easy and usually requires the use of specialized equipment. Let's begin by examining what is meant by the development properties of a photoresist, and how to measure them.

The goal of exposing a resist with an aerial image is to use a spatial variation in exposure energy (the aerial image) to create a spatial variation in dissolution properties, that is, a solubility differential. For a positive resist, exposed areas of the resist become soluble in developer, the unexposed areas remain insoluble. In a real situation, however, there are no totally exposed or unexposed regions -- only various degrees of partial exposure. Thus, the "exposed" part of the resist will have a higher dissolution rate than the "unexposed" part. As one might expect, it is the variation of the rate of dissolution with exposure dose that determines the most critical aspect of the photoresist development properties.

Development rate is defined as the change in the position of the resist/developer interface with time during the development process, and in general it is a vector with both magnitude and direction. To make this rate easy to measure (and to think about), consider a flat resist on a flat wafer that is uniformly exposed over a large area. When developed, the development rate will occur in only one direction (down) and the development rate of the resist will be exactly (except for the sign) equal to the change in the resist thickness with time. Thus, a real-time method of measuring thin film thickness could be used to measure the development rate of a photoresist. Such an instrument is, quite appropriately, called a Development Rate Monitor (DRM).

Suppose that a DRM is used to measure the development rate of a resist which has been exposed at some set dose. Although the measurement may seem straightforward, interpreting the results is far from simple. As we saw in the last several editions of this column, it is not the exposure dose incident on the resist which causes a change in the development rate, but the dose which actually makes it into the resist that matters. Reflections from the resist and substrate and absorption within the resist means that the actual exposure dose deposited in the resist is different from the incident dose and, in fact, can vary considerably from the top to the bottom of the resist. The result is a variation in development rate with depth into the resist that must be correlated with the variation in exposure dose in order to gain useful information from the data. If this is done properly, the result will be a plot of resist development rate as a function of exposure dose as shown in Figure 1.

Typically, plots of development rate versus exposure are shown on log-log scales for several reasons. First, historically, log-log plots have been used in characterizing photographic materials since the first publication of this behavior in 1890 by Hurter and Driffield [1]. As such, these curves are often called Hurter-Driffield curves or H-D curves. Second, log-log plots tend to be more physically revealing. On the exposure scale, variations in exposure caused by the aerial image are relative to the nominal dose. For example, the exposure dose at the edge of a chrome line may be 30% of the nominal dose. Relative variations are best represented on a logarithmic scale. On the development side, a logarithmic scale tends to be more physically significant. A 5 nm/s change in development rate will have little significance in the exposed part of the resist, but will have a significant impact on the unexposed resist dissolution rate. The log-development rate scale weights the lower development rates more heavily.

What does the development rate H-D curve tell us about resist performance? Since the goal of our exposure was to create a dissolution rate differential between exposed and unexposed parts of the resist, it would seem logical that the greater the dissolution rate differential the better. We want the development rate under the clear portions of the mask to be as high as possible, while at the same time keeping the development rate under the chrome portions of the mask as low as possible. Obviously, changes in the shape of the development rate H-D curve will affect the dissolution rate differential in the imaged photoresist. For this reason, resist designers spend a significant portion of their efforts trying to change the shape of the resist H-D curve.

Can the "goodness" of a resist be quantified based on the shape of its H-D curve? There are several possible metrics which can be defined. Based on the above discussion, one might choose the ratio of the development rate for completely exposed resist (R_{max}) to the development rate for unexposed resist (R_{min}), called the *total development rate ratio*. Figure 1 shows a resist with a total development rate ratio of 200. Although one would expect that increasing the total development rate ratio would improve the development performance of a resist, this is not always true. Remember that an imaged resist is partially exposed everywhere. The "dark" regions of the resist always receive some exposure, and the "bright" regions are never fully exposed. Thus, the variation in development rate resulting from an infinite variation in exposure dose does not match closely with actual experiences. A modification of the total development rate ratio would be to consider the ratio of development rates for a set exposure range which more closely matches the range of exposures experienced by photoresist during imaging. A 4X range of exposure has been shown to describe most typical imaging situations (the dose at the edge of a line is about four times lower than the dose at the center of the clear area) [2].

On a log-exposure scale, a 4X exposure range has a constant width. This constant width exposure range can now be moved back and forth on the H-D curve in order to find the maximum development rate ratio over this range. We shall call this the *4X development rate ratio*. Figure 2 shows the same H-D curve with the 4X development rate ratio identified, which has a value of about 40. Here, the non-linearity of modern photoresists becomes apparent. A 4X change in exposure produces a 40X change in development rate! As an aside, by finding the position of the 4X exposure band which maximizes the 4X development ratio, we have, by default, also found the optimum exposure dose for this resist.

Finally, a third metric to judge the quality of the development rate curve can be used -- the much abused and maligned *photoresist contrast, g*. Quite simply, the photoresist contrast is the maximum slope of the development rate H-D curve [3].

$$g \equiv \left. \frac{\P \ln R}{\P \ln E} \right|_{\max} \tag{1}$$

As can be seen from the H-D curve, a larger slope should, in general, result in a larger 4X development rate ratio and better photoresist performance. But, as with the total development rate ratio, high contrast does not *necessarily* mean a larger 4X development rate ratio, though it typically does. The contrast of the H-D curve of Figure 1 is about 3.

The value of using contrast to describe a photoresist's capabilities lies in a simple algebraic rearrangement of its definition:

$$\frac{\P \ln R}{\P x} = g \frac{\P \ln I}{\P x} \tag{2}$$

Equation (2) is called the *lithographic imaging equation* because it quite simply summarizes the basic principle of lithography. The left hand side of the lithographic imaging equation describes the spatial variation in development rate. As we have said, it is our goal to create a large spatial variation in development rate. The right hand side of the equation includes the photoresist contrast and a term called the log-slope of the aerial image. The *image log-slope* describes the quality of the aerial image and, as one might expect, determines the exposure range that the photoresist must respond to. Thus, the solubility differential is determined by the quality of the image (the image log-slope) and the quality of the photoresist (the photoresist contrast).

There are many well-known problems associated with using photoresist contrast, but they all have to do with the way in which contrast is measured. A very common method for measuring contrast without the use of a DRM is to measure the relative resist thickness remaining after development as a function of exposure, as shown in Figure 3. In fact such a curve, often called the photoresist characteristic curve, is a pseudo Hurter-Driffield curve. The measured contrast is then the slope of the characteristic curve as the thickness remaining approaches zero. Unfortunately, this simple measurement technique quite frequently gives the wrong answer!

So far, our description of development has centered around the variation of development rate with exposure dose. In the next edition of this column we'll explore other issues related to development rates, including surface inhibition and the role of surfactants, and explain why the simple characteristic curve measurement of photoresist contrast often fails to give accurate results.

References

1. F. Hurter and V. C. Driffield, "Photochemical Investigations and a New Method of Determination of the Sensitiveness of Photographic Plates," *Journal of the Society of the Chemical Industry* (May 31, 1890) pp. 455-469.

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3. C. A. Mack, "Lithographic Optimization Using Photoresist Contrast," *KTI Microlithography Seminar, Proc.*, (1990) pp. 1-12, and *Microelectronics Manufacturing Technology*, Vol. 14, No. 1 (Jan. 1991) pp. 36-42.

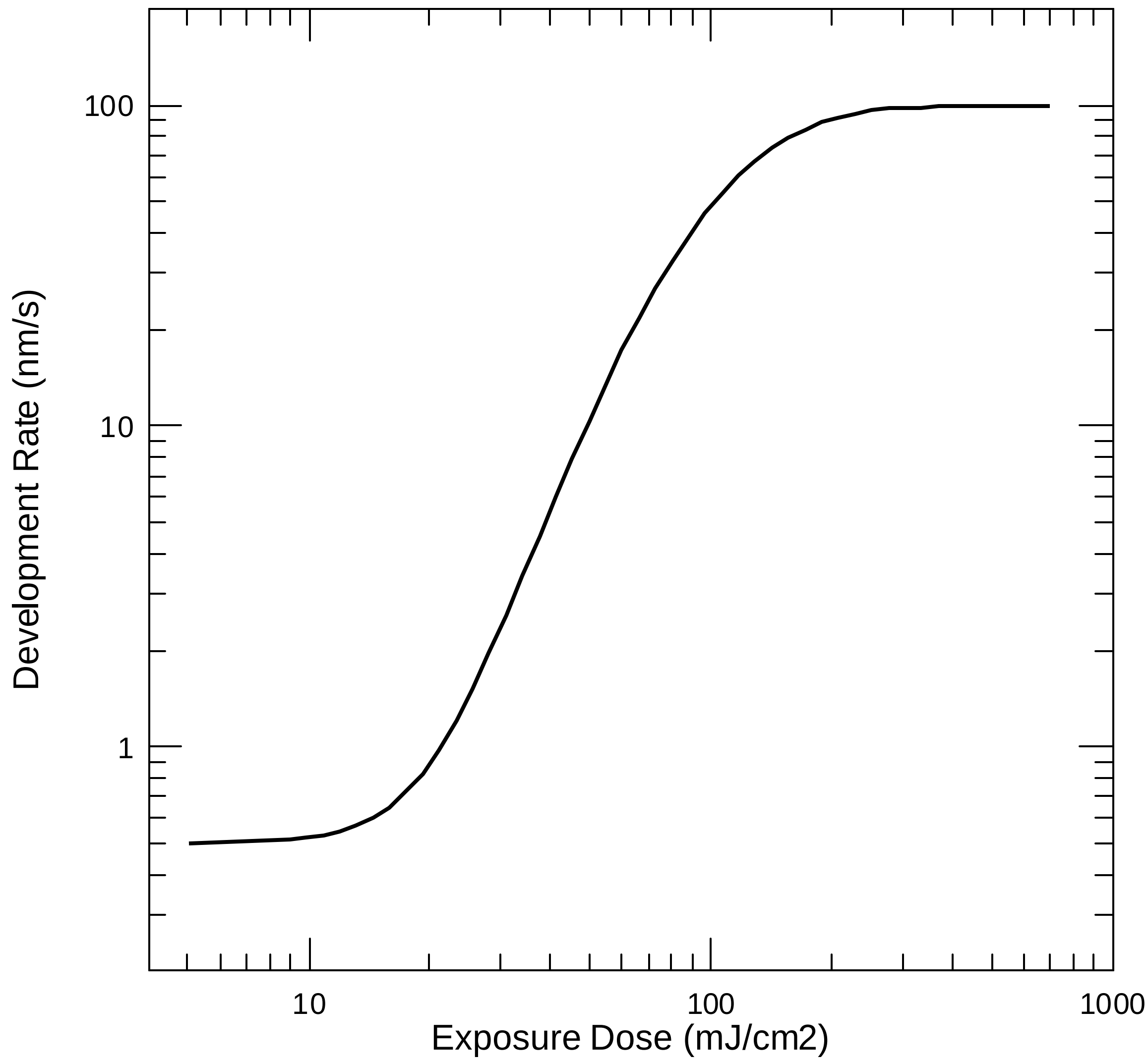

Figure 1. Typical development rate function of a positive photoresist (one type of Hurter-Driffield curve).

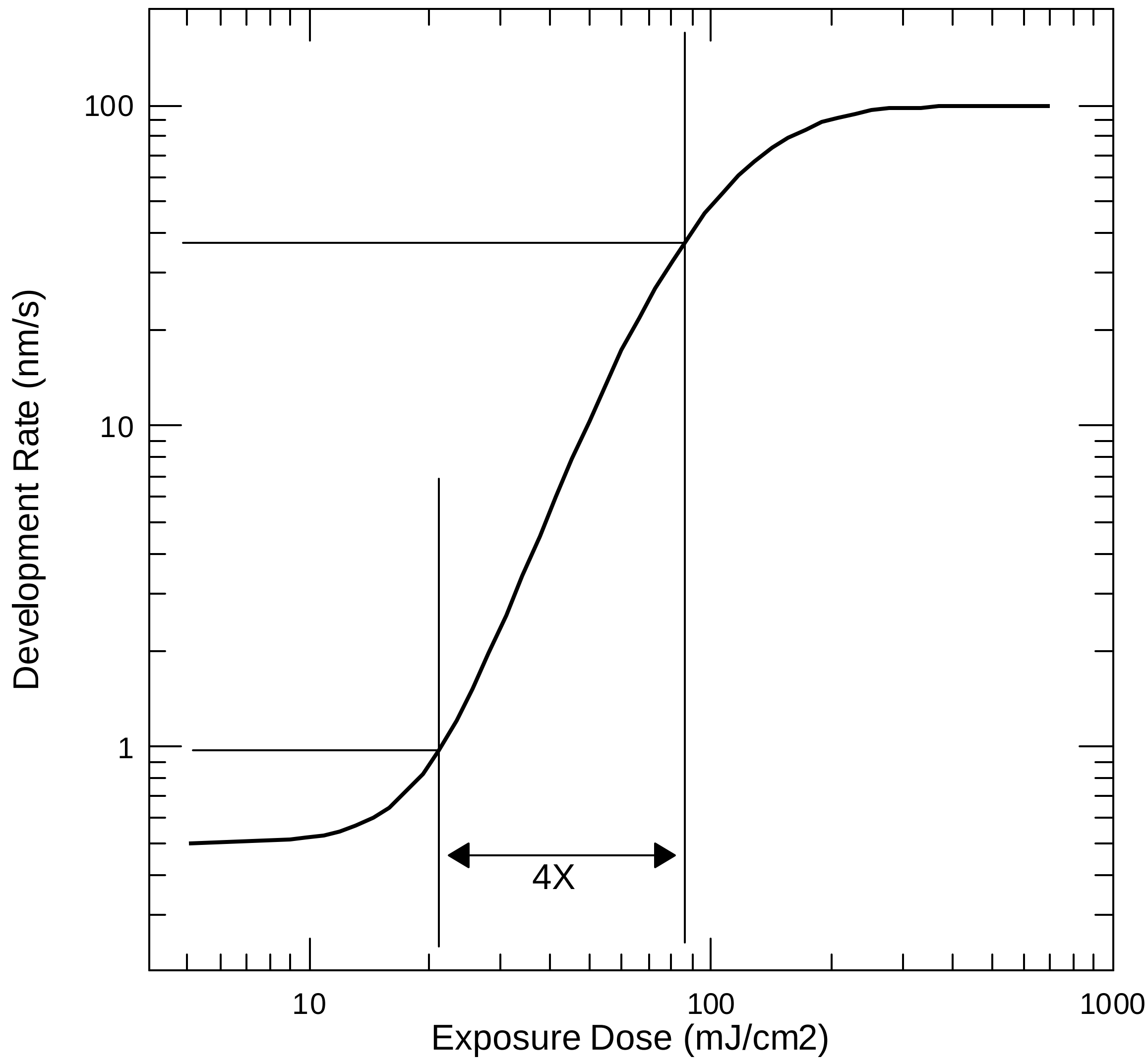

Figure 2. Hurter-Driffield curve showing the 4X development rate ratio.

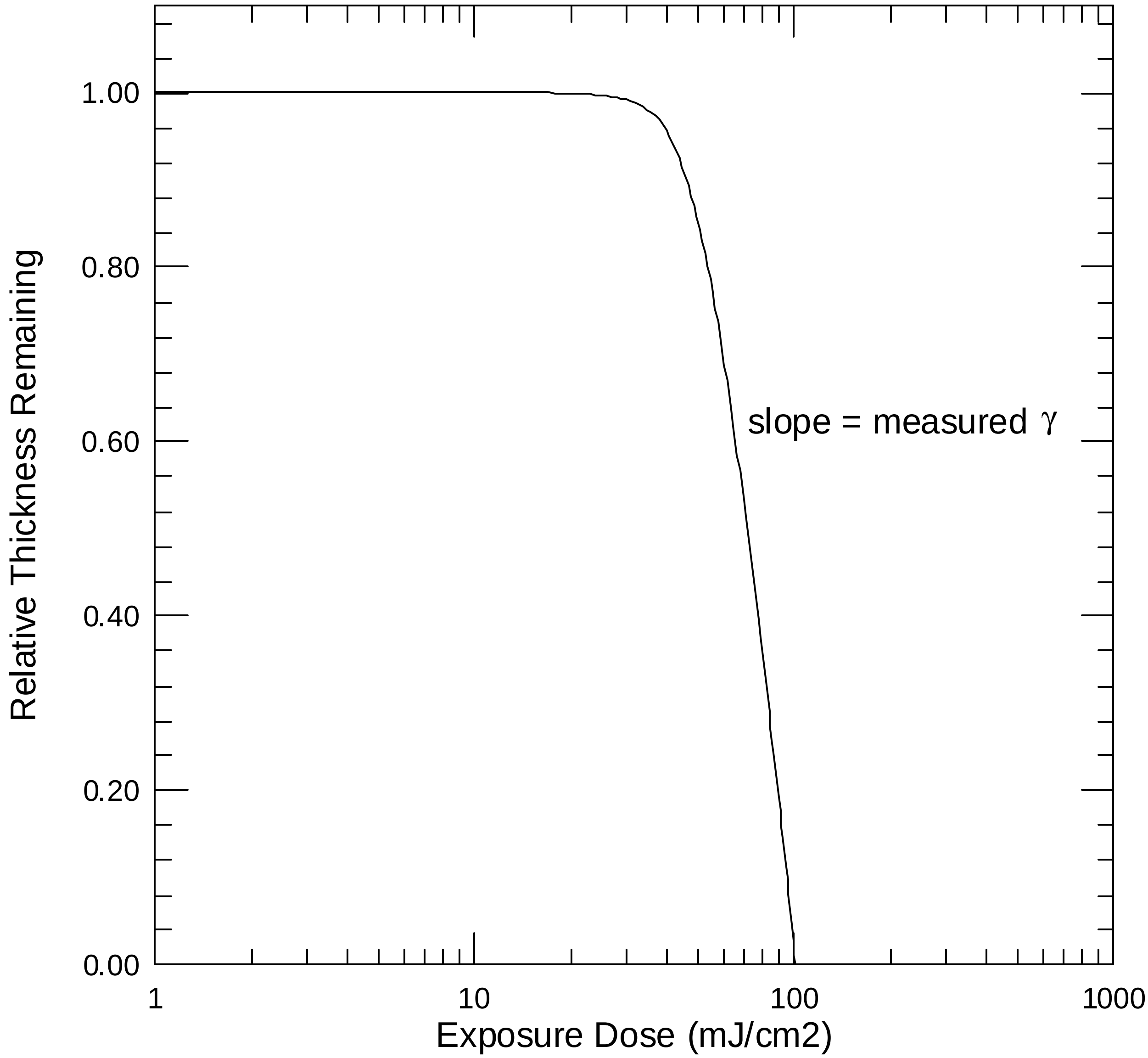

Figure 3. Measured contrast using the photoresist characteristic curve of relative thickness remaining after development as a function of exposure.