

# Photoresist Development, part 2

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In the last edition of the column we discussed the importance of development and described the major attribute of a photoresist -- its variation of development rate with exposure dose. In the process we defined a number of possible metrics to judge the quality of a photoresist based on this variation. The *total development rate ratio* is defined as the ratio of the maximum development rate (completely exposed positive resist) to the minimum development rate (completely unexposed resist). The larger the ratio, the better the resist. However, the true range of exposures used in imaging is far less than from zero to infinite dose. Thus, a more appropriate metric was defined: the *4X development rate ratio* is the maximum ratio of development rates over a 4X range of exposure doses. This ratio is most easily visualized by plotting development rate versus exposure dose on a log-log scale. Finally, a theoretical definition of the *photoresist contrast*,  $g$ , was given:

$$g \equiv \frac{\int \ln R}{\int \ln E} \Big|_{\max} \quad (1)$$

As we will see, this definition of contrast allows us to determine when the conventional measurement technique for contrast (the characteristic curve of resist thickness remaining versus dose for open frame exposures) fails to give an accurate measure.

Although exposure dose is quite obviously the controlling variable for a resist's development rate, there are other factors which affect the dissolution properties of a resist. In particular, measurement of the development rate of a photoresist reveals a variation of development rate with depth into the photoresist which is independent of exposure dose variations. Quite often, the top surface of the photoresist develops more slowly than the bulk resist for the same level of exposure. This effect is called *surface inhibition* or surface induction [1]. For some resist/developer combinations the opposite may occur where the top surface development rate is higher than the bulk. A typical example of surface inhibition is shown in Figure 1.

There are several possible causes of surface inhibition. Unlike the bulk of the resist, the top surface is in contact with the environment. During softbake or at any time between softbake and develop, the top surface of the resist may interact chemically with the environment. The most obvious possible reaction is an oxidation of the resist in contact with air. For chemically amplified resists, base contaminants may neutralize photogenerated acids at the top of the resist. The result is typically a reduction of the development rate for the resist exposed to the atmosphere. Also, residual solvent left in the resist after spin coat and bake tends to increase the development rate of the resist. The very

process of spin coating and hotplate baking produces a gradient of solvent from top to bottom of the resist film [2]. The top of the photoresist is solvent poor, resulting in a reduced development rate. Finally, properties of the developer itself can cause surface inhibition.

When development moved from batch-based to track-based methods in the early 1980s, a problem with development uniformity emerged. The resist, being quite hydrophobic, tends to repel the aqueous based developer like water on a waxed car. The result is “hot spots” of fast development where the developer beaded on the resist. To solve this problem, track-based developers employ *surfactants*, surface acting agents which reduce the surface tension of the developer and improve wetting of the resist surface. Surfactants are typically long chain hydrocarbons with an ionic salt on one end. The long hydrocarbon gives one end of the molecule an “oily” nature (and thus solubility in organic solvents) while the salt gives the other end a polar nature (and thus solubility in polar solvents like water). Common surfactants include ammonium lauryl sulfate (the active ingredient in shampoo) and quarternary ammonium salts (a typical first generation surfactant for developers).

While surfactants such as those described above have the ability to reduce the surface tension of a developer and improve the wetting of the resist, there is a potential side effect. Most of the surfactants used for developers, with the exception of some of the more recently developed materials, coat the resist surface immediately as the developer is applied. The result is good wetting, but now the developer is separated from the resist by a thin layer of surfactant. Surface inhibition results.

With surfactant laden developers solving the wetting problems of the early track-based spray development systems, an interesting new problem arose. To characterize the behavior of these new developers, the conventional technique for measuring photoresist contrast was employed [3]. Interestingly, the surfactant developers had significantly higher measured contrast than similar developers without surfactant. In fact, by using more effective surfactants the measured contrast could be made arbitrarily large. Lithographic performance, however, did not keep pace with the rise in contrast. In fact, photoresists with contrast values in excess of 100 did not show improved resolution or process latitude over resists with more moderate values (under 5). What was happening? The conventional technique for measuring contrast -- resist thickness remaining versus dose for open frame exposures -- failed to give an accurate measure of the true contrast, as defined in equation (1).

When a resist has strong surface inhibition, higher exposure is required to break through the slowly developing surface. The result is an over-exposure of the bulk resist, leading to a high development rate. When the development does break through the surface, it rushes through the overexposed bulk resist to reach the bottom. The result is a characteristic curve of thickness versus log dose which is virtually independent of the bulk properties of the resist and only dependent on the surface inhibition effects. In the presence of surface inhibition, the measured contrast can be significantly greater than the actual bulk contrast [4]. In fact, the conventional measurement technique gives an accurate value of the contrast only when the development rate of the photoresist does not vary significantly from the top to the bottom of the resist. This is extremely important since it is the bulk contrast (the theoretical contrast) which determines the resist’s imaging characteristics.

Another way of looking at the difference between the actual bulk contrast of a resist and that measured by the thickness versus energy curve is to consider the *path of development*. Development rate is a vector, with both magnitude and direction. The characteristic curve measures the actual vertical dissolution, but combines both exposure effects (of primary importance) and surface inhibition effects (of much lesser importance). Why is the vertical dissolution not directly related to lithographic quality? Consider a typical development path as shown in Figure 2. The path can be generated by tracing the position of the resist surface through the development time. Although the path begins vertically, a photoresist image is formed when the path turns to a nearly horizontal direction. It is the behavior of the horizontal development path that determines the behavior of the resist profile (including the final dimension of the feature and the resist sidewall angle). As one might expect, the horizontal path is strongly affected by the exposure dose variation caused by the aerial image but is not affected by surface inhibition.

The substrate can also influence the development properties of a resist. Any chemical interaction between the photoresist and the substrate will undoubtedly affect the dissolution properties of the resist at the substrate (usually slowing the rate down). Further, the mechanics of spin coating may actually cause a gradient in molecular weight which may result in an enhancement of the development rate at the substrate (seen as microgrooves at the bottom of the resist profile). These effects are much less understood (and less frequently observed) than bulk or surface effects. Finally, development into high aspect ratio holes (such as contacts) implies that mass transport (of developer into the hole and dissolved resist out of the hole) may play a critical role in the proper formation of the feature. Needless to say, the chemistry and mechanisms of photoresist dissolution remains one of the most important topics of lithography research.

## References

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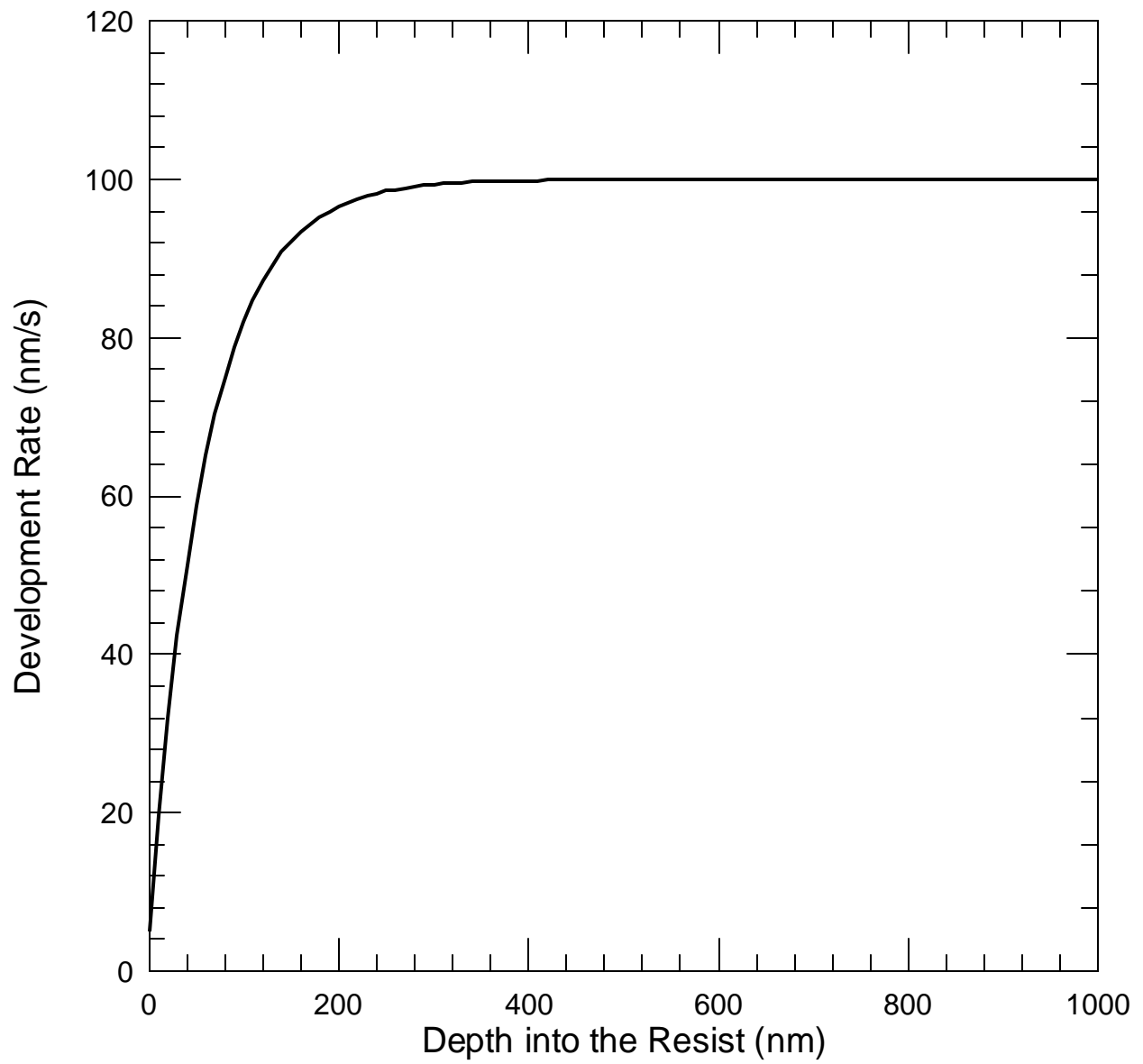


Figure 1. Typical example of a development rate function showing surface inhibition -- the reduction of the development of the top surface of the resist relative to the bulk.

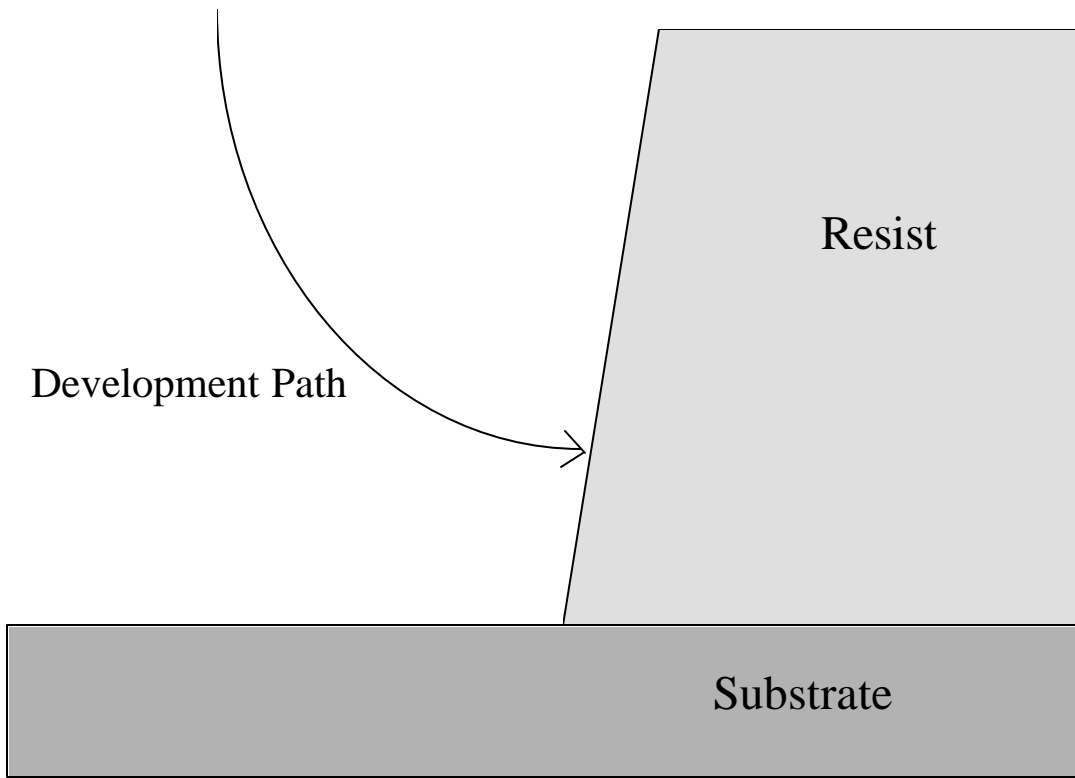


Figure 2. Typical development path starts out vertically, but ends up nearly horizontal by the end of the development cycle.