Notch Model for Photoresist Dissolution

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I. INTRODUCTION

Simulation of the optical microlithography process used in the fabrication of semiconductor integrated circuits began in the mid 1970s [1,2], and has progressed greatly since then [3-5]. One important part of every lithography model is a description of the development process. In particular, a development model must predict the development rate of a photoresist as a function of the chemical composition of the resist. (The chemical composition of the resist is intentionally modified by selective exposure of the photoresist to light). The original Dill development rate model [2] was an empirical curve fit of experimental development rate data. The three parameters for the model had no physical significance and the model fit the data only over a limited range. The Kim model [6] was proposed to improve the fit over the full range of data. The model was again empirical, but at least one of the three parameters had some physical significance. The author proposed two kinetic models for development [7,8] which will be briefly described below. These four and five parameter models are based on proposed chemical mechanisms for the effects of the various chemical species on the development rate. The advantage of the kinetic models are that all of the parameters have physical significance and thus the lithographic behavior of the photoresist can be correlated with the chemical mechanism giving rise to that behavior. However, the true mechanisms of development are undoubtedly more complicated than the simple ones used to generate these development models, which thus still retain a certain empirical nature.

Recent experimental development rate data has shown that current models do not give satisfactory agreement with the data for some high resolution i-line photoresists [9]. In particular, a "notch" exhibited in the dissolution rate versus photoactive compound (PAC) concentration curve had dramatic influence on the lithographic response of several photoresists but was not well fit by current models. This paper modifies an existing kinetic model to provide a semi-empirical relationship which accurately fits experimental data.

II. BACKGROUND

A typical diazonaphthoquinone (DNQ) positive photoresist has two basic components. The bulk of the photoresist (typically 70% by weight) is made up of a novolac resin. By itself, the resin is moderately soluble in the aqueous base used as a developer. The remaining portion of the resist is a photoactive compound (PAC). Upon exposure to light, the photoactive compound is transformed into a carboxylic acid. The PAC acts to inhibit dissolution of the resin.

On the other hand, the carboxylic acid enhances the dissolution of the resist. Thus, exposure results in a solubility change. Many other resist chemistries behave similarly.

The original Mack kinetic model for resist dissolution [7] centered around the principle of dissolution enhancement. A mixture of resin and photoactive compound is considered insoluble. By converting some of the PAC to a carboxylic acid, the dissolution rate is enhanced. The resulting model of dissolution rate as a function of relative PAC concentration, $R(m)$, which also included simple diffusion of developer to the resist surface, became

$$R = R_{max} \frac{(a+1)(1-m)^n}{a+(1-m)^n} + R_{min} \qquad (1)$$

where R_{max} is the maximum (fully exposed) dissolution rate, R_{min} is the minimum (unexposed) dissolution rate, n is the dissolution selectivity (which corresponds to the surface reaction order), and a is a simplifying constant given by

$$a = \frac{(n+1)}{(n-1)}\left(1-m_{TH}\right)^n$$

where m_{TH} is the threshold PAC concentration, defined as the point of inflection of the $R(m)$ curve. Here, unexposed resist dissolution (given by R_{min}) is assumed to occur by a separate mechanism from exposed dissolution. When the diffusion step is fast enough to be neglected, the resulting m_{TH} becomes negative and a becomes large. In this case, the dissolution model simplifies to

$$R = R_{max}(1-m)^n + R_{min} \qquad (2)$$

The above model is based on the increase of the dissolution rate by exposed PAC. An enhanced kinetic model has also been proposed [8] that describes both enhancement of the dissolution rate by exposed PAC and inhibition of the rate by the unexposed PAC. This model is given by

$$R = R_{resin} \frac{1 + k_{enh}(1-m)^n}{1 + k_{inh}(m)^l} \qquad (3)$$

where k_{enh} is the rate constant for the enhancement mechanism, n is the enhancement reaction order, k_{inh} is the rate constant for the inhibition mechanism, l is the inhibition reaction order, and R_{resin} is the development rate of the resin alone, before any enhancement or inhibition.

For no exposure, $m = 1$ and the development rate is at its minimum. From equation (3),

$$R_{min} = \frac{R_{resin}}{1 + k_{inh}} \qquad (4)$$

Similarly, when $m = 0$, corresponding to complete exposure, the development is at its maximum.

$$R_{max} = R_{resin} \ (1 + k_{enh}) \tag{5}$$

Note that the unexposed resist dissolution (and thus R_{min}) is determined by the degree of inhibition caused by the PAC rather than by a separate mechanism as was assumed in the original Mack kinetic model.

III. NEW "NOTCH" MODEL

Some recent experimentally derived $R(m)$ behavior is not well fit by either model [9]. Figure 1 shows the best fit of both the Mack and the enhanced Mack development rate models to one set of data from Ref. 9. In the region around a 0.5 PAC concentration the data exhibits a "notch" behavior where the actual development rate drops very quickly to a value much less than that predicted by either model. It was previously shown that this sudden drop in rate, resembling a "notch" in the otherwise slowly varying behavior, is critical to resist performance [9]. It seems likely that today's high contrast i-line resists have been engineered to produce this notch by default, since it produces good lithographic performance. Likewise, it is critical that a development model properly describe this region of the dissolution rate curve in order to accurately predict the behavior of the resist.

A semi-empirical model has been devised in order to better fit the notch behavior described above. This notch model begins with the simple version of the Mack model given in equation (2) and adds a notch function equivalent to the threshold behavior given by equation (1).

$$R = R_{max}(1-m)^n \left[\frac{(a+1)(1-m)^{n\_notch}}{a+(1-m)^{n\_notch}} \right] + R_{min} \tag{6}$$

where

$$a = \frac{(n\_notch+1)}{(n\_notch-1)}\left(1 - m_{TH\_notch}\right)^{n\_notch}$$

The term in the brackets of equation (6) provides the notch-like behavior where m_{TH_notch} is the position of the notch along the PAC concentration axis and n_notch gives the strength of the notch. This is illustrated in Figures 2 and 3. Note that the five parameter notch model of equation (6) reverts to the original Mack model of equation (1) when $n = 0$.

IV. CONCLUSIONS

A new model for photoresist dissolution rate as a function of photoactive compound concentration has been presented. This semi-empirical model combines elements of previous kinetic models in order to better fit recent experimental dissolution rate behavior. In particular,

rate data exhibiting a dissolution "notch" can be well fit by this model. Since the shape of the dissolution rate function near the notch effectively controls the lithographic performance of the resist, accurate matching of the model to this part of the data is critical.

V. ACKNOWLEDGEMENTS

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Development Rate (nm/s)
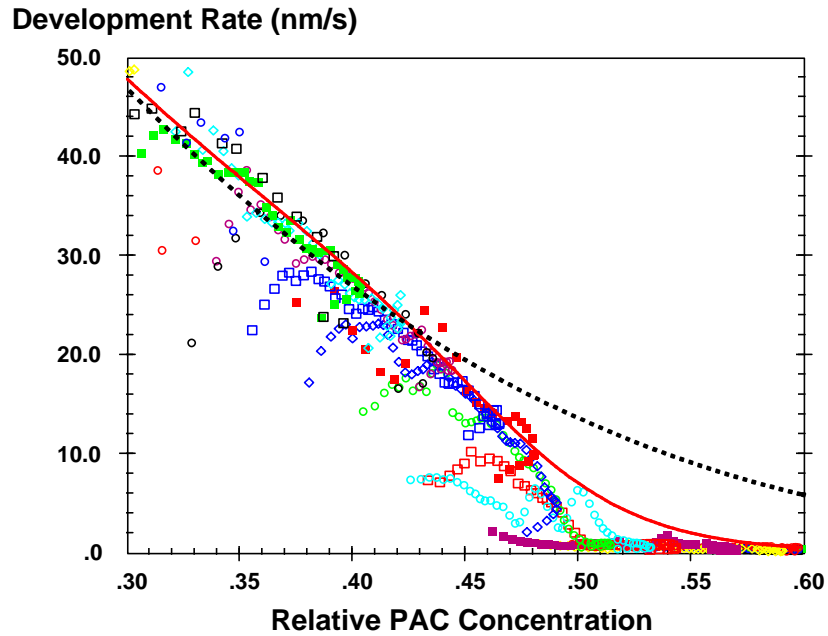
Figure 1. Comparison of experimental dissolution rate data (symbols) exhibiting the so-called "notch" shape to best fits of the Mack (dotted line) and enhanced Mack (solid line) models [from Ref. 9]. The data shows a steeper drop in development rate at about 0.5 relative PAC concentration than the models predict.

Development Rate (nm/s)
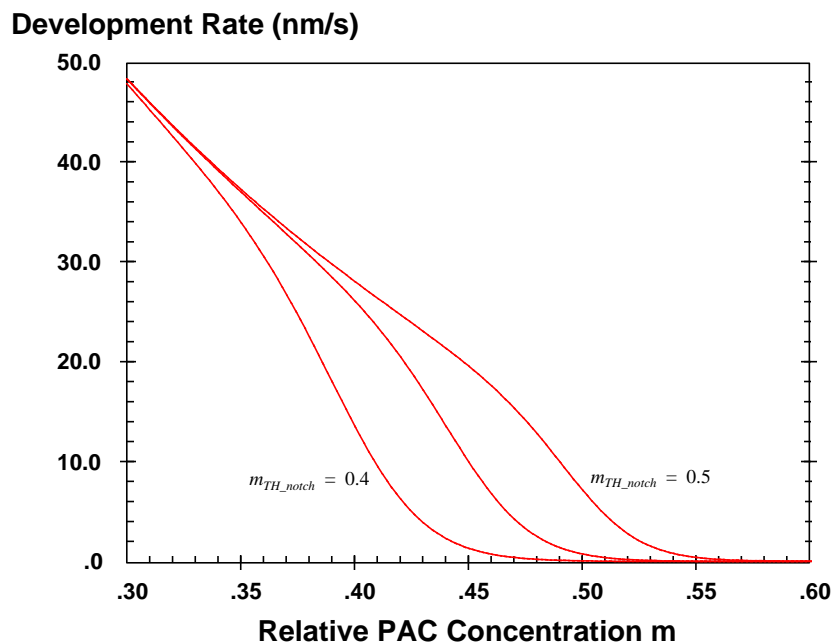
Figure 2. Plots of the notch model for m_{TH_notch} equal to 0.4, 0.45, and 0.5 and n_notch equal to 30.

Development Rate (nm/s)

n_notch = 15

n_notch = 60

Relative PAC Concentration m
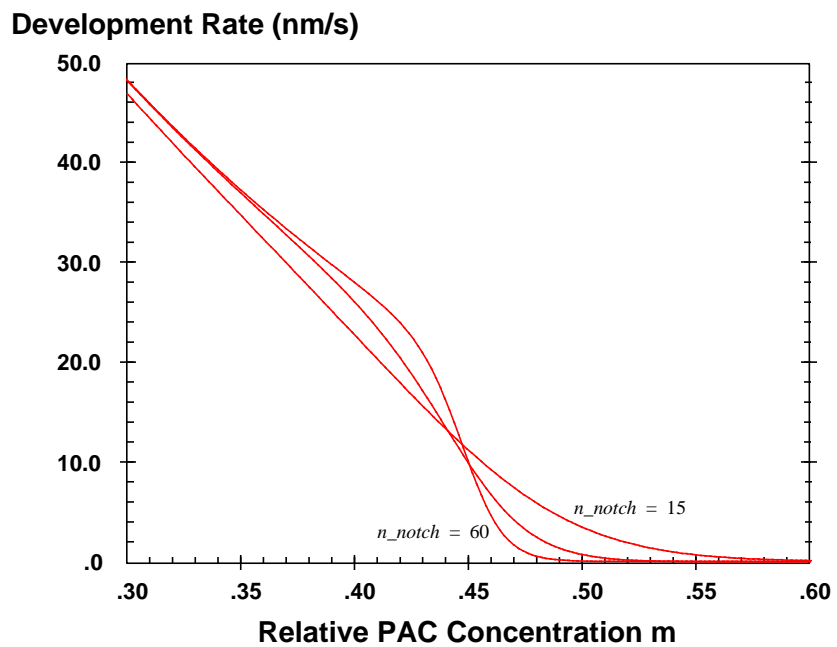
Figure 3. Plots of the notch model for *n_notch* equal to 15, 30, and 60 and m_{TH_notch} equal to 0.45.