Technical Note

A Criterion for Case II Diffusion in Resist Development by Dissolution

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The development of a polymeric resist by dissolution may be described as a two-step process (1). First, the smaller solvent molecules must diffuse into the polymer matrix. The resulting increase in internal pressure causes the rigid, interpenetrating polymer molecules to loosen and swell. The increased mobility of the polymer molecules typically causes an increase in the mobility of the solvent molecules, in which case the diffusive penetration of the solvent will autoaccelerate. Second, the polymer molecules become sufficiently separated from each other to diffuse into the solvent.

Since the mobility of the solvent molecules depends upon both the concentration of the solvent and the length of time the polymer molecules have been loosening, the diffusion step generally cannot be described by Fick's law unless the diffusion coefficient has both a concentration and history dependence. There are other effects which add to the difficulty of developing a widely applicable, theoretical model of the development process, such as surface induction (2) and adhesion (3). Because of the complication arising from these effects, the development process is usually described by an empirical model in which a bulk development rate is modified to include the necessary depth dependence (3-4).

One type of development behavior that appears to be very non-Fickian is Case II or relaxation-balanced diffusion, in which the solvent polymer interface travels into the polymer at a constant velocity with little diffusion of solvent beyond the interface (Fig. 1). The dissolution of PMMA by MIBK, a resist-solvent combination frequently used in electron-beam lithography, is probably the most important example of this behavior.

Model and Solution

For Case II diffusion, a one-dimensional model of the solvent-polymer system will be considered (Fig. 2). The solvent concentration c in the polymer is described by

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad [1]$$

where the diffusivity is assumed to be constant and may be taken as the smallest value possible in the polymer for use in the criterion to be developed. The assumption of constant D is valid for this system because the solvent concentration is too small to have a significant effect on D except at the solvent-polymer interface. The concentration profile resulting after an induction period is approximated by

$$c(x, o) = c_o e^{-\beta x} \qquad [2]$$

where c_o is the solvent concentration at which dissolution occurs and β is a positive parameter to be determined. The initial condition is given by Eq. [2] since time will be measured from the beginning of dissolution instead of from the initial exposure of polymer to solvent. One of the boundary conditions is that c approaches zero as x tends to infinity

$$c(\infty, t) = 0 \qquad [3]$$

The flux at the liquid-solid interface, which moves at a constant velocity (dissolution rate) V, is a combination of the mass transfer from the bulk solvent to the interface and the amount (rate) of solvent replenished into the bulk solvent due to the dissolution of polymer

$$D\frac{\partial c}{\partial x} = -k_m(c_b - c_s) + Vc \quad \text{at } x = Vt \qquad [4]$$

where k_m is the mass transfer coefficient, c_b is the concentration in the bulk solvent, and c_s is the concentration in the fluid at the interface. The solvent concentration in the polymer at the interface is in equilibrium with c_s or the fluid phase concentration such that $c = K_e c_s$ where K_e is the equilibrium constant. Use of the relationship in Eq. [4] yields

$$D\frac{\partial c}{\partial x} = (h + V)c - K_m; \quad h \equiv k_m/K_e, \quad K_m \equiv k_m c_b \quad \text{at } x = Vt \qquad [5]$$

The boundary value problem is recast with the following coordinate transformation (5)

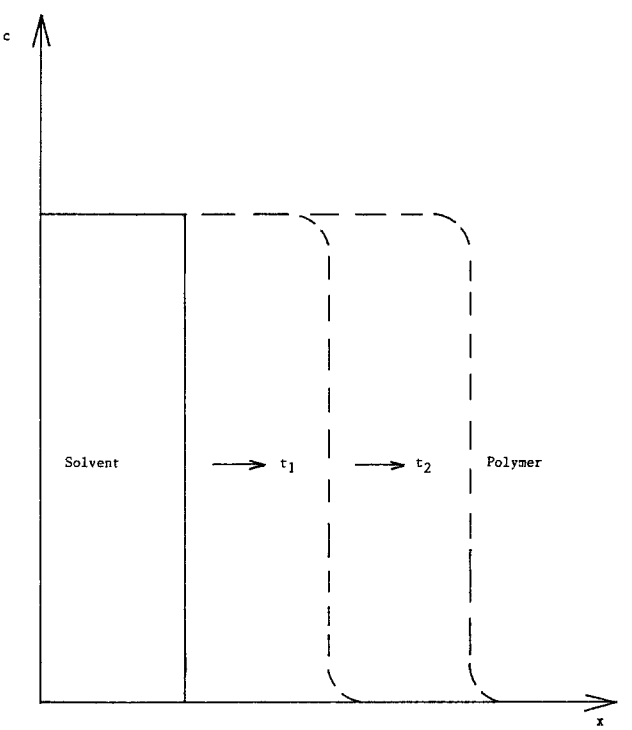

Fig. 1. Solvent concentration C vs. distance x for Case II diffusion. The dotted lines represent the profiles at times t_1 and t_2; $0 < t_1 < t_2$.

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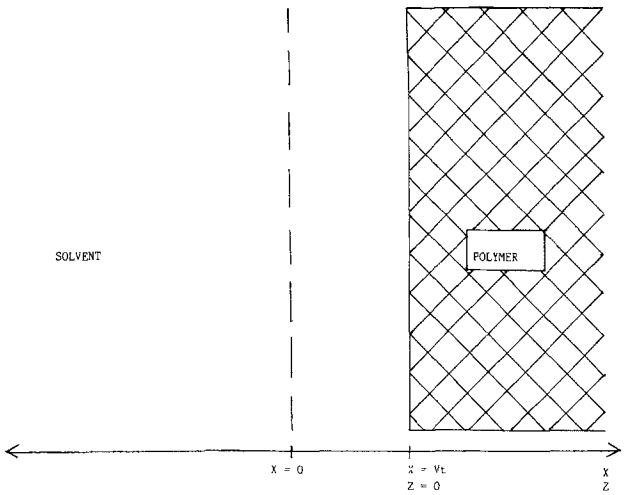

Fig. 2. Coordinates for one-dimensional model. For the case depicted, a slice of thickness *Vt* has been etched away.

$$z = x - Vt \qquad [6]$$

which transforms Eq. [1], [2], [3], and [5] to

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} + V\frac{\partial c}{\partial z} \qquad [7]$$

$$c = c_o e^{-\beta z} \quad \text{at } t = 0 \qquad [8]$$

$$c = 0 \quad \text{as } z \to \infty \qquad [9]$$

$$D\frac{\partial c}{\partial z} = (h + V)c - K_m \quad \text{at } z = 0 \qquad [10]$$

The solution of Eq. [7] may be obtained by separation of variables to give

$$c = \left(A \exp\left\{-\left[\frac{V}{2D} - \left(\frac{v^2}{4D^2} + \frac{\lambda}{D}\right)^{1/2} z\right\} + B \exp\left\{-\left[\frac{V}{2D} + \left(\frac{V^2}{4D^2} + \frac{\lambda}{D}\right)^{1/2}\right] z\right\}\right) \exp(\lambda t) \qquad [11]$$

where λ is the separation constant and A and B are constants. Use of the boundary conditions yields

$$c = \left(\frac{K_m}{h + 2V}\right) \exp(-Vz/D) = c_o \exp(-Vz/D) \qquad [12]$$

A comparison of Eq. [12] with [8] shows that

$$c_o = \frac{K_m}{h + 2V}, \quad \beta = V/D \qquad [13]$$

Thus, the solvent concentration in polymer is given by Eq. [12] where $z = x - Vt \geqq 0$.

Criterion

The question at hand is the condition under which the dissolution takes place in a shell-progressive manner. This shell-progressive dissolution takes place and thus a sharp interface boundary would exist if the solvent concentration in the polymer approaches zero at a very small distance from the interface. If one insists the solvent concentration at a small penetration depth S into the polymer to be less than 1% of c_o, *i.e.*, $c/c_o \leqq 0.01$ at $z = S$ (or $x = Vt + S$), it follows from Eq. [12] that

$$\frac{VS}{D} \geqq 4.6 \qquad [14]$$

since $\exp(-4.6)$ is 0.01.

The criterion given by Eq. [14] is a very simple and yet useful result that can be used to determine whether the desired pattern fidelity can be obtained within the specified penetration depth S. If S is specified as 10Å, for example, a sharp, well-defined pattern should emerge within the tolerance of 10Å with a sharp boundary. Note that the dissolution rate V has to be adjusted in accordance with the requirement of Eq. [14] for the sharp boundary, and that the minimum value of D for the solvent-polymer system of interest should be used.

An alternate form of the criterion for Case II diffusion may be obtained from Eq. [13] and [14]

$$c_b \geqq \frac{c_o}{k_m}\left(\frac{9.2D}{S} + h\right) \qquad [15]$$

where the definition of $K_m(=k_m c_b)$ has been used. This relationship shows explicitly how the penetration depth is related to the material properties and bulk solvent concentration. For systems in which measurement of S is impractical, a conservative estimate of c_b may be obtained by using

$$S = \frac{D}{V} \qquad [16]$$

The criterion of Eq. [15] with the equality can be used for two different purposes. First, it can be used to experimentally determine the parameters k_m and $h(=k_m/k_e)$. If experiments are carried out in which the bulk solvent concentration is varied and the penetration depth is determined at which the concentration becomes 1% of c_o, a linear plot of c_b *vs.* S should yield the values of the parameters. Note that the penetration depth for this purpose may be defined at any fraction of c_o, or approximated by Eq. [16], provided the constant (9.2 in Eq. [15]) is correspondingly reset. Second, the criterion may be used to compare the degree to which a solvent-polymer system exhibits case II behavior.

Summary

A criterion for development which proceeds by Case II diffusion has been derived. The criterion depends only upon material parameters, the easily controlled bulk concentration of solvent, and the penetration depth which may be calculated or specified by the user. By specifying the value of the penetration depth, the user can easily determine conditions under which development proceeds at the desired rate for a system exhibiting this behavior.

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