Kinetic model for solid diffusion with a competing surface reaction*

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A microscopically-motivated model of solid diffusion with a competing chemical reaction is defined and analyzed. In appropriate limits these results reduce to standard expressions. This model corresponds well to observed experimental results for diffusion of Zn into Pb, and example curves are exhibited based on parameters appropriate to the Zn in Pb system.

I. INTRODUCTION

Most work in solid-state diffusion with diffusant plated on a surface considers only Gaussian concentration profiles

$$c(x,t) = [S_0/(\pi Dt)^{1/2}]e^{-x^2/4Dt}, \tag{1}$$

where S_0 is the thickness of diffusant initially plated on the surface of the specimen, D is the diffusivity, and $c(x,t)$ is atomic fraction of the diffusant at (x,t). This expression is appropriate if the diffusion anneal is long compared to $\pi S_0^2/4Dc_s^2$, where c_s is the solubility of the diffusant.[1,2]

In some systems, this condition cannot be met. For example, in the study of the diffusion of zinc into lead,[3,4] it was found that surface oxidation led to back-diffusion and "humped" concentration profiles, rather than Gaussian profiles, for long diffusion times. In that work, short diffusion time experiments were performed, leading to the well-known erfc solution of the diffusion equation

$$c(x,t) = c_s \,\text{erfc}[x/(4Dt)^{1/2}]. \tag{2}$$

In addition, the humped profiles were analyzed[4,5] by assuming a surface chemical reaction term in the diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - Wc\delta(x), \tag{3}$$

where W is taken to be a constant. The solution of this equation for initial condition $c(x,0) = S_0\delta(x)$ is

$$c(x,t) = \frac{S_0 e^{-x^2/4Dt}}{(\pi Dt)^{1/2}}\left[1 - W\left(\frac{\pi t}{4D}\right)^{1/2}e^{(Wt+x)^2/4Dt}\right.$$
$$\left.\times \,\text{erfc}\left(\frac{Wt+x}{(4Dt)^{1/2}}\right)\right]. \tag{4}$$

The present work was undertaken in order to study these diffusion processes in a microscopically-motivated model which correctly includes the effects of surface chemical reactions as well as diffusion for arbitrarily short or long times.

II. KINETIC MODEL

We consider a model in which the solid is described by a spatially-varying potential seen by a diffusing atom. The surface is represented by a potential barrier (from outside) of height $E_0 + E_1$, as shown in Fig. 1.

The diffusing atoms obey the diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{5}$$

with initial condition, $c(x,0) = 0$, $x > 0$; and with boundary condition $J(0,t) = -D(\partial c/\partial x)_{x=0} = j(t)$, where $j(t)$, the surface flux, is the difference between the flux in and the flux out

$$j(t) = M(t)\nu a_0 e^{-\beta(E_1+E_0)} - c(0,t)\nu a_0 e^{-\beta E_1}. \tag{6}$$

In this expression, the flux in is the product of a vibrational frequency ν, the distance between the first atomic layer of the crystal and the layer of diffusant immediately outside the crystal a_0, a Boltzmann factor for the surface barrier, and $M(t)$, the number of diffusant atoms available in the layer just outside the crystal measured relative to the number of sites in the first atomic layer of the crystal. If we define t_0 as the time at which only one layer of diffusant atoms is left at the surface, then

$$M(t) = \begin{cases} \dfrac{N}{N_0} \equiv \alpha, & t \le t_0 \\[2mm] \alpha\Lambda(t), & t \ge t_0, \end{cases} \tag{7}$$
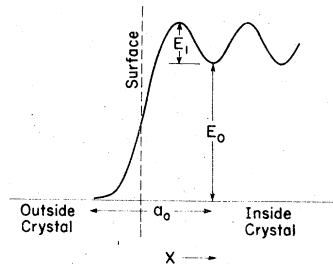

FIG. 1. Qualitative model for the potential energy seen by a diffusing atom near the surface of the crystal.

where N is the average number of diffusant atoms per unit area in a full layer in the plated film; N_0 is the number of lattice sites per unit area in the first atomic layer of the crystal; α is of order unity; and $\Lambda(t)$ is the average number of layers in the plated film.

The flux out, in Eq. (6), is the product of ν, a_0, a Boltzmann factor for the energy barrier shown in Fig. 1, and the concentration immediately inside the crystal.

The time dependence of $\Lambda(t)$ remains to be specified: $N\Lambda(t)$ is the total number of diffusant atoms per unit area in the surface film at time t, so if the chemical reaction at the surface is proportional to the number of exposed diffusant atoms, we can write

$$\frac{d}{dt} N\Lambda(t) = -\frac{KNM(t)}{\alpha} - j(t)\frac{N_0}{a}, \tag{8}$$

where K is taken to be constant [and will, of course, be related to W in Eq. (3), above]. K/α represents the reaction term which removes diffusant atoms from the diffusion process. Furthermore, the initial condition for $\Lambda(t)$ is $\Lambda(0) = S_0/a$, where a is the separation between atomic layers in the diffusant film. (From here on, we will assume

$a_0 \cong a$ and $\alpha \cong 1$.)

The solubility of the diffusant, c_s is defined by the condition $c(0,t) = c_s$, when $j(t) = 0$ with $S_0 \to \infty$. So, from Eq. (6),

$$c_s = e^{-\beta E_0}. \tag{9}$$

III. SOLUTION OF DIFFUSION PROBLEM

It is easy to show that $c(x,t)$ is given by the following expression when the surface flux is known[6]:

$$c(x,t) = \frac{1}{\sqrt{\pi D}} \int_0^t dt' \frac{j(t-t')e^{-x^2/4Dt'}}{\sqrt{t'}}. \tag{10}$$

We will consider the solutions for $t \le t_0$ and $t \ge t_0$.

1. $t \le t_0$

If $t \le t_0$, $M(t) = 1$, so $c(x,t)$ is given by the integral equation

$$c(x,t) = \frac{1}{\sqrt{\pi \tau}} \int_0^t dt' \frac{e^{-x^2/4Dt'}}{\sqrt{t'}} [c_s - c(0, t-t')], \tag{11}$$

where $\tau \equiv D/\nu^2 a^2 e^{-2\beta E_1}$. Eq. (11) is a convolution-type integral equation which can easily be solved by Laplace transforms. The exact result is

$$c(x,t) = c_s \left\{ \text{erfc}[x/(4Dt)^{1/2}] - e^{-x^2/4Dt} \exp\left[(t/\tau)^{1/2} + \frac{x}{(4Dt)^{1/2}} \right]^2 \text{erfc}\left[(t/\tau)^{1/2} + \frac{x}{(4Dt)^{1/2}} \right] \right\}, \quad (t \le t_0). \tag{12}$$

The parameter τ can be estimated for the diffusion of metals into lead: $2E_1 \cong 0.75$ eV for interstitial motion ($2E_1 \cong 1.0$ eV for substitutional motion), $\nu \cong 2 \times 10^{12}$ sec^{-1}, $a^2 \cong 10^{-15}$ cm^2. Taking $\beta \cong 20$ eV^{-1} (near the melting point of lead), we obtain $\tau \cong D \times 10^{-3}$ sec (D in cm^2/sec). This is an extremely short time, only 7×10^{-10} sec at 300°C for the diffusion of Zn in Pb.[3,4] Physically, τ represents the time required to reach the solubility limit just inside the surface of the crystal.

For all practical times $t \gg \tau$, the second term in the bracket in Eq. (12) can be neglected, so that $c(x,t)$ reduces to Eq. (2), as expected, for $t \le t_0$.

The time t_0 is defined by

$$\Lambda(t_0) = 1. \tag{13}$$

When $t \le t_0$, Eq. (8) for $\Lambda(t)$ becomes

$$\frac{d\Lambda}{dt} = -K - \gamma e^{t/\tau} \text{erfc}(t/\tau)^{1/2}, \tag{14}$$

where $\gamma \equiv c_s \nu e^{\beta E_1}$. This equation, too, is easily solved either by Laplace transforms or by direct integration, from which we obtain

$$\Lambda(t) = \frac{S_0}{a} - Kt - \gamma\tau \left(e^{t/\tau} \text{erfc}(t/\tau)^{1/2} - 1 + \frac{2}{\sqrt{\pi}} (t/\tau)^{1/2} \right). \tag{15}$$

When there is no surface reaction, $K = 0$, and when $t_0 \gg \tau$, we obtain from Eqs. (13) and (15),

$$t_0 = (\pi/4\gamma^2\tau)(S_0/a - 1)^2 = \pi(S_0 - a)^2/4Dc_s^2, \quad (K = 0). \tag{16}$$

This equation is equivalent to that obtained by Malkovich.[1] For general values of K, when $t_0 \gg \tau$, we find

$$t_0 = \frac{\gamma^2\tau}{K^2\pi} \left[\left(1 + \frac{\pi K(S_0 - a)}{a\gamma^2\tau}\right)^{1/2} - 1 \right]^2. \tag{17}$$

The parameter γ can be estimated for the same conditions we used to estimate τ. We obtain $\gamma \cong 10^9 c_s$ sec^{-1}. For Zn in Pb at 300°C, $\gamma \cong 3 \times 10^6$ sec^{-1}, and $\gamma\tau \cong 2 \times 10^{-3}$. Physically, γ represents the probability per unit time of an atom immediately outside the crystal jumping inside.

2. $t \geq t_0$

If $t \geq t_0$, $c(x,t)$ is determined by the following coupled equations:

$$c(x,t) = \frac{c_s}{(\pi\tau)^{1/2}} \int_0^{t_0} dt' \frac{e^{-x^2 4D(t-t')}}{(t-t')^{1/2}} e^{t'/\tau} \operatorname{erfc}\left(\frac{t'}{\tau}\right)^{1/2}$$

$$+ \frac{c_s}{(\pi\tau)^{1/2}} \int_{t_0}^t dt' \frac{e^{-x^2/4D(t-t')}}{(t-t')^{1/2}} \left[\Lambda(t') - \frac{c(0,t')}{c_s}\right],$$

(18)

$$\frac{d\Lambda}{dt} \doteq -(\gamma+K)\Lambda(t) + \frac{\gamma}{c_s} c(0,t).$$

(19)

If $\psi(x,s)$ is the Laplace transform of $c(x,t+t_0)$, we obtain the following exact Laplace transform of the solution to Eqs. (18) and (19):

$$\psi(x,s)$$

$$= G(x,s) - \frac{c_s K}{\sqrt{\tau}} \frac{e^{-x\sqrt{s}/\sqrt{D}}}{s\left[s^{3/2} + s/\sqrt{\tau} + \sqrt{s}\,(\gamma+K) + K/\sqrt{\tau}\,\right]}$$

$$+ c_s e^{-x\sqrt{s}/\sqrt{D}} e^{st_0} \operatorname{erfc}(st_0)^{1/2}$$

$$\times \left(\frac{1}{s} - \frac{\gamma}{\sqrt{s}\,[s^{3/2} + s/\sqrt{\tau} + \sqrt{s}\,(\gamma+K) + K/\sqrt{\tau}\,]}\right),$$

(20)

where $G(x,s)$ is the Laplace transform of

$$g(x,t) \equiv \frac{c_s}{(\pi\tau)^{1/2}} \int_0^{t_0} dt' \frac{\exp[-x^2/4D(t+t_0-t')]}{(t+t_0-t')^{1/2}}$$

$$\times e^{t'/\tau} \operatorname{erfc}(t'/\tau)^{1/2}.$$

(21)

The function $g(x,t-t_0)$ is closely related to the integral obtained by Malkovich[1] for $c(x,t)$ when $t_0 < t$, namely,

$$c_M(x,t) \equiv \frac{2c_s}{\sqrt{\pi}} \int_{x/(4Dt)^{1/2}}^\infty e^{-y^2} \operatorname{erf}\left[y\left(\frac{t_0}{t-t_0}\right)^{1/2}\right] dy.$$

(22)

When $t - t_0 \gg \tau$, we can show that

$$g(x,t-t_0) = c_M(x,t) + O((\tau/t)^{1/2}).$$

(23)

IV. DISCUSSION

The model and its solution presented above include the physical effect of finite initial surface flux, leading to the result that finite time is required to reach the solubility limit just inside the surface of the crystal. This time, however, is the extremely short time τ, which can be neglected for all practical purposes in the metallic systems we have considered.

After a time of order τ, the model leads to the erfc concentration profile up to the time when the
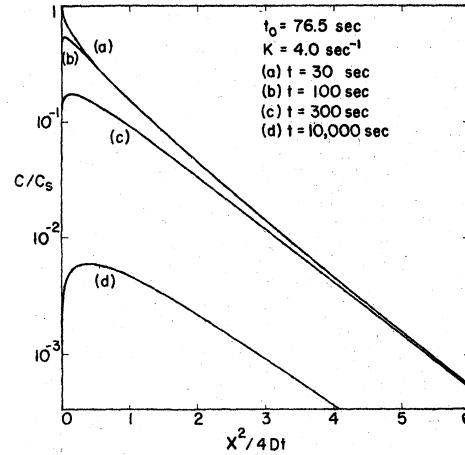

FIG. 2. Concentration profiles as a function of anneal time for a system with a surface chemical reaction competing with the diffusion process. Parameters are typical of those obtained experimentally for the diffusion of Zn into Pb.

surface layer of diffusant is depleted, just as one expects. However, after the surface layer is depleted, at times $t > t_0 + \tau$, the solution is more complicated. We obtain the Malkovich result,[1] $c(x,t) = c_M(x,t)$, when $K = 0$, as expected. When $K \neq 0$, we obtain humped concentration profiles as shown in Fig. 2. In this figure we have used values of the parameters typical of those obtained for humped concentration profiles for the diffusion of Zn in Pb at $300\,°C$: $D = 7.3 \times 10^{-7}$ cm^2/sec, $c_s = 2.6 \times 10^{-3}$, $S_0/a = 1000$, $K = 4.0$ sec^{-1}.

In the limit of long times, $t \gg t_0$, we can approximately invert Eq. (20), and using the Gaussian approximation to $c_M(x,t)$ appropriate in this limit, we obtain

$$c(x,t) \cong \frac{2}{\pi} c_s \left(\frac{t_0}{\tau}\right)^{1/2} e^{-x^2/4Dt} \left[1 + \frac{K}{2\gamma}\left(\frac{\pi t_0}{\tau}\right)^{1/2}\right]$$

$$\times \left\{1 - \frac{K}{\gamma}\left(\frac{\pi t}{\tau}\right)^{1/2} \exp\left[\frac{x}{(4Dt)^{1/2}} + \frac{K}{\gamma}\left(\frac{t'}{\tau}\right)^{1/2}\right]^2\right.$$

$$\left. \times \operatorname{erfc}\left[\frac{x}{(4Dt)^{1/2}} + \frac{K}{\gamma}\left(\frac{t}{\tau}\right)^{1/2}\right]\right\}.$$

(24)

Comparing this expression to Eq. (4), it is clear that we should identify W in Eq. (3) with $2K(D/\tau)^{1/2}/\gamma$.

If we consider concentration profiles in which the total anneal time t, is fixed, but K and S_0 are allowed to vary, we obtain curves very much like those of Fig. 2: When $K = 0$, the concentration profile changes smoothly from the erfc form to the Gaussian form as S_0 is decreased. As the surface reaction term ($K \neq 0$) is added, the profiles show

pronounced humps when S_0 is small enough that $t > t_0$.

The surface concentration $c(0, t)$, is interesting to consider on the time-scale τ. $c(0, t)$ approaches the saturation solubility initially in a time of order τ, as indicated by Eq. (12). The initial rise in $c(0, t)$ is proportional to $(t/\tau)^{1/2}$. After time t_0, $c(0, t)$ continues to rise toward c_s as $(t - t_0)/t_0$ for a time of order τ until the final layer of diffusant on the surface is depleted. Then, when $t - t_0 \gg \tau$, $c(0, t)$ descends as $(2/\pi) c_s \tan^{-1} [t_0/(t - t_0)]^{1/2}$ for $K = 0$, which is the Malkovich result.[1] When $K \gg \gamma$ $(\tau/t)^{1/2}$ and $t \gg t_0$,

$$c(0, t) \cong c_s \frac{\gamma^2 \tau \sqrt{t_0}}{\pi K^2 t^{3/2}} \left[1 + \frac{K}{2\gamma} \left(\frac{\pi t_0}{\tau} \right)^{1/2} \right]. \qquad (25)$$

These results correspond well to the experimental observations for the diffusion of Zn into Pb.[3,4] They provide a basis for understanding the crossover, observed in that system, from erfc to humped concentration profiles. This calculation also provides a microscopically-motivated model of solid-state diffusion which offers insight into the processes governing the concentration profiles of more macroscopic diffusion models like Eq. (3).

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