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# Some moving-boundary problems arising from a model for solid-state diffusion

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**Abstract.** In this paper we formulate and analyse moving-boundary problems arising from the dissociative model for impurity diffusion in a semiconductor. We consider one-dimensional surface-source and implant problems and two-dimensional diffusion under a mask edge. The diffused profiles which result exhibit a number of novel features.

**Key words:** moving boundary, diffusion, semiconductor, impurity, mask edge

## 1. Introduction

This paper is concerned with some moving-boundary problems arising from the dissociative model for impurity diffusion. The dissociative mechanism is of substitutional-interstitial type, the impurity existing mainly in the substitutional state (*i.e.* occupying lattice sites), but diffusing only in its interstitial form. In the dissociative mechanism an interstitial impurity atom becomes substitutional by occupying a vacancy (an empty lattice site). This mechanism has been used to describe many solid-state diffusion systems, including copper in germanium and zinc in gallium arsenide (see, for example, Frank and Turnbull [1], Sturge [2] and Meere *et al.* [3], to which we refer for further details of the mechanism). The appropriate equations are given in one dimension by

$$\frac{\partial s}{\partial t} = -k_{dL}s + k_{dR}iv, \qquad \frac{\partial}{\partial t}(s+v) = D_v\,\frac{\partial^2 v}{\partial x^2}, \qquad \frac{\partial}{\partial t}\,(s+i) = D_i\,\frac{\partial^2 i}{\partial x^2}, \tag{1}$$

where $s(x,t), v(x,t)$ and $i(x,t)$ are the concentrations of the substitutional impurity atoms, lattice vacancies and interstitial impurity atoms, respectively. The surface of the semiconductor corresponds to $x = 0$, while $x > 0$ is its interior. The constants $D_v$ and $D_i$ are the diffusivities for the vacancies and interstitials, respectively, and $k_{dL}$ and $k_{dR}$ are reaction constants for the dissociative mechanism.

We shall be considering the solution to (1) subject to two sets of boundary and initial conditions. We first consider a surface-source problem for which the boundary and initial conditions are given by

$$\begin{array}{lll} i = i^*,\ v = v^* & \text{on} & x = 0, \\ i \to 0,\ v \to v^* & \text{as} & x \to +\infty, \\ s = 0,\ i = 0,\ v = v^* & \text{at} & t = 0, \end{array} \tag{2}$$

where the constants $i^*$ and $v^*$ are the surface concentration of interstitial impurity and the equilibrium vacancy concentration, respectively. We introduce the quantity

$$s^* = \frac{k_{dR} i^* v^*}{k_{dL}}$$

and consider the solution to (1) and (2) for the case $i^* = O(v^*)$ with $v^* \ll s^*$. This limit represents a physically relevant parameter regime and we shall show in Section 2 how it gives rise to a moving-boundary problem, which we then solve analytically.

In Section 3 we consider the solution to (1), subject to boundary and initial conditions appropriate to an implant diffusion. These are given by

$$\begin{aligned}
&\frac{\partial i}{\partial x} = 0,\ v = v^* && \text{on} \quad x = 0, \\
&\frac{\partial i}{\partial x} \to 0,\ \frac{\partial v}{\partial x} \to 0 && \text{as} \quad x \to +\infty, \\
&s = 0,\ i = F(x),\ v = v^* && \text{at} \quad t = 0,
\end{aligned} \tag{3}$$

where $v^*$ is again the equilibrium vacancy concentration. We ignore implant damage effects. These conditions can model an implant diffusion with $F(x) \geq 0$ being the initial distribution of implanted interstitial impurity. We shall scale the substitutional and interstitial concentrations by $i_m$, where

$$i_m \equiv \max_{x \geq 0} F(x),$$

and for the problem considered here we assume that

$$i_m > v^*, \tag{4}$$

so that there are regions where the concentration of implanted impurity exceeds the equilibrium vacancy concentration. In the limit we consider, which is equivalent to that studied in Section 2, an interstitial impurity atom tends to turn substitutional as soon as it finds a vacancy. This property implies that interstitials and vacancies will not coexist at the same location and leads to a moving-boundary problem, with moving boundaries separating regions of negligible interstitial concentration from those of negligible vacancy concentration. We derive the appropriate moving-boundary formulation for this implant problem and discuss some special solutions together with more general qualitative properties. A related, but more complex problem of this type was considered in Meere [4] in which the substitutional atoms were allowed to diffuse by a vacancy mechanism.

Section 4 is concerned with the corresponding limit of a two-dimensional surface-source problem describing diffusion under a mask edge. We conclude in Section 5 with some discussion.

It should be noted that, while we shall refer to semiconductor applications throughout, models of the type discussed here are much more generally applicable to (for example) chemical reactions in which two mobile species ($i$ and $v$) react reversibly to form an immobile product ($s$).

## 2. The surface-source problem

### 2.1. Formulation and boundary-layer analysis

We consider the solution to (1) subject to (2). We non-dimensionalise the equations as follows:

$$\overline{s} = \frac{s}{s^*},\ \overline{v} = \frac{v}{v^*},\ \overline{i} = \frac{i}{i^*},\ \overline{t} = \frac{t}{T},\ \overline{x} = \frac{x}{\sqrt{D_i T}},$$

where $T$ is some representative time scale. The non-dimensional problem is now

$$\begin{array}{lll} \mu\,\dfrac{\partial s}{\partial t} = -s + iv, & \dfrac{\partial}{\partial t}(\omega s + \varepsilon v) = \beta\varepsilon\,\dfrac{\partial^2 v}{\partial x^2}, & \dfrac{\partial}{\partial t}(s + \varepsilon i) = \varepsilon\,\dfrac{\partial^2 i}{\partial x^2}, \\ i = 1,\ v = 1 & \text{on} \quad x = 0, & \\ i \to 0,\ v \to 1 & \text{as} \quad x \to +\infty, & \\ s = 0,\ i = 0,\ v = 1 & \text{at} \quad t = 0, & \end{array} \tag{5}$$

where

$$\mu = 1/k_{dL}T,\ \varepsilon = i^*/s^*,\ \beta = D_v/D_i \quad \text{and} \quad \omega = i^*/v^*$$

and where we have dropped the overbars. For the remainder of this section we assume that $\mu$ is negligible and hence replace $(5)_1$ by

$$s = iv. \tag{6}$$

The solution to the problem is then self-similar with

$$s = s(x/t^{\frac{1}{2}}),\ v = v(x/t^{\frac{1}{2}}),\ i = i(x/t^{\frac{1}{2}}).$$

We now discuss the case $\varepsilon \ll 1$. In this limit there is a boundary layer at $\widehat{x} = O(1)$ where $x = \varepsilon^{\frac{1}{2}}\widehat{x}$, and in $\widehat{x} = O(1)$ we pose

$$s \sim \widehat{s}_0(\widehat{x}, t),\ v \sim \widehat{v}_0(\widehat{x}, t),\ i \sim \widehat{i}_0(\widehat{x}, t).$$

The leading-order equations in $\widehat{x} = O(1)$ are

$$\widehat{s}_0 \ = \ \widehat{i}_0\widehat{v}_0, \qquad \omega\,\frac{\partial \widehat{s}_0}{\partial t} = \beta\,\frac{\partial^2 \widehat{v}_0}{\partial \widehat{x}^2}, \qquad \frac{\partial \widehat{s}_0}{\partial t} = \frac{\partial^2 \widehat{i}_0}{\partial \widehat{x}^2}, \tag{7}$$

and $(7)_2$ and $(7)_3$ imply that (from the boundary conditions on $x = 0$)

$$\omega\widehat{i}_0 - \beta\widehat{v}_0 = \omega - \beta. \tag{8}$$

We note that in the linear term $a(t)x$, which would in general appear on the right-hand side of (8), we must have $a(t) = 0$ in order to match into an outer region discussed below. It then follows that

$$\begin{aligned} \widehat{i}_0 \ &= \ \{((\omega - \beta)^2 + 4\omega\beta\widehat{s}_0)^{\frac{1}{2}} + \omega - \beta\}/2\omega, \\ \widehat{v}_0 \ &= \ \{((\omega - \beta)^2 + 4\omega\beta\widehat{s}_0)^{\frac{1}{2}} - \omega + \beta\}/2\beta \end{aligned} \tag{9}$$

and we obtain the single nonlinear diffusion equation

$$\frac{\partial \widehat{s}_0}{\partial t} = \beta\,\frac{\partial}{\partial \widehat{x}}\left(((\omega - \beta)^2 + 4\omega\beta\widehat{s}_0)^{-\frac{1}{2}}\,\frac{\partial \widehat{s}_0}{\partial \widehat{x}}\right). \tag{10}$$

Equation (10) is to be solved subject to

$$\widehat{s}_0 = 1 \quad \text{on} \quad \widehat{x} = 0, \qquad \widehat{s}_0 \to 0 \quad \text{as} \quad \widehat{x} \to +\infty, \qquad \widehat{s}_0 = 0 \quad \text{at} \quad t = 0, \tag{11}$$

which complete the specification of the leading-order boundary-layer problem.

We now need to distinguish between the cases $\beta > \omega$ and $\beta < \omega$, the behaviour of these two cases being qualitatively different. It is clear from (9) and (11) that if $\beta > \omega$ then

$$\widehat{v}_0 \to 1 - \omega/\beta, \; \widehat{i}_0 \to 0 \quad \text{as} \quad \widehat{x} \to +\infty, \tag{12}$$

whereas for $\beta < \omega$

$$\widehat{v}_0 \to 0, \; \widehat{i}_0 \to 1 - \beta/\omega \quad \text{as} \quad \widehat{x} \to +\infty. \tag{13}$$

We note that, as shown by (12)–(13), the inner solutions need not (and do not) satisfy the conditions of (5) as $x \to +\infty$, because of the additional regions described below. A physical interpretation of this behaviour is as follows. In $x = O(1)$ the substitutional concentration $s$ is expected to be small, since not enough vacancies are initially available for $s$ to be of $O(1)$. It then follows from (6) that either $i$ or $v$ must also be small. If there are sufficient vacancies initially available, or if they are able to diffuse sufficiently fast into a region of vacancy depletion, then we may expect that $v$ will remain $O(1)$. The preceding analysis indicates that the condition for this is that $\beta > \omega$, *i.e.* that $D_v v^* > D_i i^*$. Conversely, if $D_i i^*$, then the impurity interstitials diffuse sufficiently rapidly and in sufficient numbers that the vacancy concentration is greatly depleted and we shall see that $v = O(\varepsilon)$ then holds in $x = O(1)$.

We now discuss the various cases in turn.

## 2.2. $\beta > \omega$

In $x = O(1)$ we have that $s$ and $i$ are exponentially small, but $v = O(1)$ and we write

$$v \sim v_0(x, t)$$

to obtain the leading-order problem

$$\frac{\partial v_0}{\partial t} = \beta \frac{\partial^2 v_0}{\partial x^2},$$
$$v_0 = 1 - \omega/\beta \quad \text{on} \quad x = 0, \qquad v_0 \to 1 \quad \text{as} \quad x \to +\infty, \qquad v_0 = 1 \quad \text{at} \quad t = 0,$$

where we have obtained the boundary condition on $x = 0$ from matching with (12), which gives the outer limit of the inner solution. Hence

$$v_0 = 1 - \frac{\omega}{\beta} \operatorname{erfc}\left(\frac{x}{2\sqrt{\beta t}}\right). \tag{14}$$

## 2.3. $\beta < \omega$

### 2.3.1. *Introduction*

In this case the asymptotic analysis leads to a moving-boundary problem. Denoting the moving boundary by $x = q(t;\varepsilon)$, we find that for $x = O(1)$ we have

for $\quad 0 < x < q(t;\epsilon): \quad s = O(\varepsilon),\; v = O(\varepsilon),\; i = O(1);$
for $\quad x > q(t;\varepsilon): \quad v = O(1)$ with $s$ and $i$ exponentially small.

For $x < q$ we write $s = \varepsilon\tilde{s}$, $v = \varepsilon\tilde{v}$ with

$$\tilde{s} \sim \tilde{s}_0(x,t),\ \tilde{v} \sim \tilde{v}_0(x,t),\ i \sim i_0(x,t)$$

and obtain

$$\tilde{s}_0 = i_0\tilde{v}_0, \qquad \frac{\partial \tilde{s}_0}{\partial t} = 0, \tag{15}$$

$$\frac{\partial i_0}{\partial t} = \frac{\partial^2 i_0}{\partial x^2}, \tag{16}$$

and for $x > q$

$$v \sim v_0(x,t)$$

with

$$\frac{\partial v_0}{\partial t} = \beta\,\frac{\partial^2 v_0}{\partial x^2}. \tag{17}$$

To complete the specification of the moving-boundary problem coupling (16) and (17), we must now consider a transition layer $x = O(1)$, where $x = q(t;\varepsilon) + \varepsilon^{\frac{1}{2}}z$. This analysis will also be relevant later in the paper.

### 2.3.2. *The transition-layer structure*

We write

$$q \sim q_0(t),\ s \sim \varepsilon s_0^\dagger(z,t),\ v \sim \varepsilon^{\frac{1}{2}} v_0^\dagger(z,t),\ i \sim \varepsilon^{\frac{1}{2}} i_0^\dagger(z,t) \tag{18}$$

for $z = O(1)$ and hence obtain

$$s_0^\dagger = i_0^\dagger, v_0^\dagger, \qquad -\omega\dot{q}_0\,\frac{\partial s_0^\dagger}{\partial z} = \beta\,\frac{\partial^2 v_0^\dagger}{\partial z^2}, \qquad -\dot{q}_0\,\frac{\partial s_0^\dagger}{\partial z} = \frac{\partial^2 i_0^\dagger}{\partial z^2}, \tag{19}$$

where $\dot{q}_0 \equiv \mathrm{d}q_0/\mathrm{d}t$. We now define

$$S^-(t) \equiv \lim_{z\to-\infty} s_0^\dagger \tag{20}$$

and, using $s_0^\dagger, i_0^\dagger \to 0$ as $z \to +\infty$ and $v_0^\dagger \to 0$ as $z \to -\infty$, we have

$$-\omega\dot{q}_0(s_0^\dagger - S^-) = \beta\,\frac{\partial v_0^\dagger}{\partial z}, \qquad -\dot{q}_0 s_0^\dagger = \frac{\partial i_0^\dagger}{\partial z}. \tag{21}$$

This system of ordinary differential equations may be further integrated to yield (absorbing the arbitrary translation of $z$ into the specification of $q(t;\varepsilon)$ at $O(\varepsilon)$)

$$i_0^\dagger = (2\beta S^-/\pi\omega)^{\frac{1}{2}} \exp(-\omega S^- \dot{q}_0^2 z^2/\beta) / \operatorname{erfc}(-(\omega S^-/2\beta)^{\frac{1}{2}}\dot{q}_0 z) \tag{22}$$

with

$$\beta v_0^\dagger = \omega(i_0^\dagger + S^-\dot{q}_0 z),\ \ s_0^\dagger = i_0^\dagger v_0^\dagger. \tag{23}$$

However, the required matching conditions for (16)–(17) can be deduced directly from (21) which implies that

$$\beta \left(\frac{\partial v_0}{\partial x}\right)^+ = -\omega \left(\frac{\partial i_0}{\partial x}\right)^- = \omega \dot{q}_0 (\tilde{s}_0)^-, \tag{24}$$

where we have introduced the notation

$$(u)^+ = \lim_{x\to q_0^+} u(x,t),\ (u)^- = \lim_{x\to q_0^-} u(x,t),$$

where $u$ is any function of $x$ and $t$. These expressions could alternatively be deduced directly from the conservation laws

$$\frac{\partial}{\partial t}(v - \omega i) = \frac{\partial^2}{\partial x^2}(\beta v - \omega i), \qquad \frac{\partial}{\partial t}(\tilde{s} + i) = \frac{\partial^2 i}{\partial x^2}.$$

### 2.3.3. *The moving-boundary problem*

We are now in a position to formulate our first moving-boundary problem. The quantities $i_0$, $v_0$ and $q_0$ are determined by

$$\frac{\partial i_0}{\partial t} = \frac{\partial^2 i_0}{\partial x^2}, \quad 0 < x < q_0(t); \qquad \frac{\partial v_0}{\partial t} = \beta \frac{\partial^2 v_0}{\partial x^2}, \quad x > q_0(t),$$
$$i_0 = 1 - \beta/\omega \quad \text{on} \quad x = 0, \qquad i_0 = 0 \quad \text{at} \quad x = q_0^-, \qquad v_0 = 0 \quad \text{at} \quad x = q_0^+,$$
$$\beta \left(\frac{\partial v_0}{\partial x}\right)^- = -\omega \left(\frac{\partial i_0}{\partial x}\right)^+,$$
$$v_0 \to 1 \quad \text{as} \quad x \to +\infty, \qquad v_0 = 1,\ q_0 = 0 \quad \text{at} \quad t = 0.$$

Using self-similarity and writing $q_0 = \alpha\sqrt{t}$, we obtain the solution

$$i_0 = (1 - \beta/\omega)(1 - \operatorname{erf}(x/2\sqrt{t})/\operatorname{erf}(\alpha/2)), \qquad 0 < x < \alpha\sqrt{t}, \tag{25}$$

$$v_0 = 1 - \operatorname{erfc}(x/2\sqrt{\beta t})/\operatorname{erfc}(\alpha/2\sqrt{\beta}), \qquad x > \alpha\sqrt{t},$$

where the constant $\alpha$ is determined by

$$(\omega - \beta)\exp(\alpha^2/4\beta)\operatorname{erfc}(\alpha/2\sqrt{\beta}) = \sqrt{\beta}\exp(\alpha^2/4)\operatorname{erf}(\alpha/2), \tag{26}$$

which has a unique solution $\alpha > 0$ for $0 < \beta < \omega$.

The substitutional concentration $\tilde{s}_0$ is determined from

$$\frac{\partial \tilde{s}_0}{\partial t} = 0, \quad 0 < x < q_0(t); \qquad \tilde{s}_0 = -\frac{1}{\dot{q}_0}\left(\frac{\partial i_0}{\partial x}\right)^- \quad \text{at} \quad x = q_0^-,$$

so that

$$\tilde{s}_0 = \frac{2(\omega - \beta)\exp(-\alpha^2/4)}{\sqrt{\pi}\alpha\omega \operatorname{erf}(\alpha/2)} \quad \text{for} \quad 0 < x < q_0(t). \tag{27}$$

In Figure 1 we plot a numerical solution for $i$ together with the corresponding leading-order asymptotic profiles in each of the regions $\widehat{x} = O(1), x = O(1)$ and $z = O(1)$.

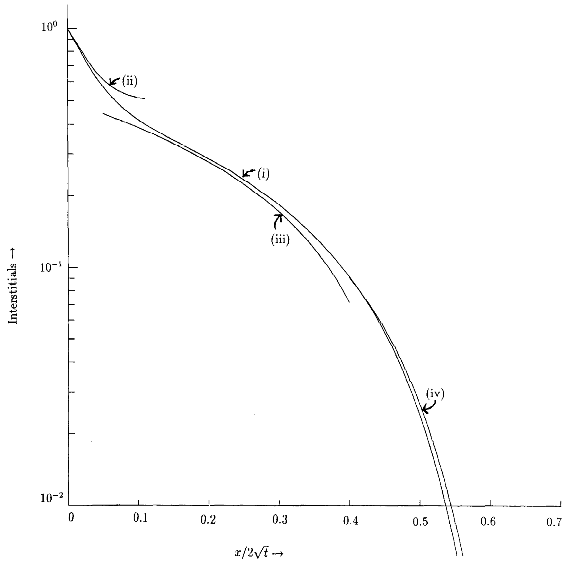


*Figure 1.*

From (26) and (27) we have

$$\alpha \sim \sqrt{\pi/\beta},\ \tilde{s}_0 \sim 2\beta/\pi\omega(\omega-\beta) \quad \text{as} \quad \beta \to \omega^-,$$

so in this limit the interface moves slowly, permitting a relatively large number of impurity atoms to become substitutional, whereas

$$\alpha \sim 2\log^{\frac{1}{2}}(\omega-\beta),\ \tilde{s}_0 \sim 1/\omega \quad \text{as} \quad \omega \to +\infty,$$

which implies in dimensional terms that $s \sim v^*$, so that the interface moves rapidly and only the vacancies which are present initially are available to be occupied by impurity.

### 2.4. $\beta = \omega$

When $\beta = \omega$, the solutions to (9)–(11) satisfy

$$\widehat{s}_0 \sim 9\widehat{x}^{-4}t^2,\ \widehat{v}_0 \sim 3\widehat{x}^{-2}t,\ \widehat{i}_0 \sim 3\widehat{x}^{-2}t \quad \text{as} \quad \widehat{x} \to +\infty. \tag{28}$$

For $x = O(1)$ we have that $s$ and $i$ are exponentially small and $v_0$ is given by (14), so that

$$v_0 = \operatorname{erf}\left(\frac{x}{2\sqrt{\beta t}}\right). \tag{29}$$

However, there is now also a transition region with $x = \varepsilon^{\frac{1}{3}}x^*$ in which we write

$$s \sim \varepsilon^{\frac{2}{3}}s_0^*(x^*,t),\ v \sim \varepsilon^{\frac{1}{3}}v_0^*(x^*,t),\ i \sim \varepsilon^{\frac{1}{3}}i_0^*(x^*,t)$$

so that

$$\frac{\partial^2 v_0^*}{\partial x^{*2}} = \frac{\partial^2 i_0^*}{\partial x^{*2}},$$

and matching with (29) and into the boundary layer $\widehat{x} = O(1)$ (in which it may be shown that

$$v - i = A(t;\varepsilon)\widehat{x} + O(\varepsilon)$$

for some $A$ which is of $O(\varepsilon^{\frac{1}{2}})$) we have

$$v_0^* - i_0^* = x^*/\sqrt{\pi\beta t}.$$

Since $s_0^* = i_0^* v_0^*$, it follows that

$$v_0^* = \frac{1}{2}\left\{\left(\frac{x^{*2}}{\pi\beta t} + 4s_0^*\right)^{\frac{1}{2}} + \frac{x^*}{\sqrt{\pi\beta t}}\right\}, \qquad i_0^* = \frac{1}{2}\left\{\left(\frac{x^{*2}}{\pi\beta t} + 4s_0^*\right)^{\frac{1}{2}} - \frac{x^*}{\sqrt{\pi\beta t}}\right\},$$

and $s_0^*$ satisfies the nonlinear, inhomogeneous diffusion equation

$$\frac{\partial s_0^*}{\partial t} = \frac{1}{2}\frac{\partial^2}{\partial x^{*2}}\left(\left(\frac{x^{*2}}{\pi\beta t} + 4s_0^*\right)^{\frac{1}{2}}\right),$$
$$s_0^* \sim 9x^{*-4}t^2 \quad \text{as} \quad x^* \to 0^+, \qquad s_0^* \to 0 \quad \text{as} \quad x^* \to +\infty, \qquad s_0^* = 0 \quad \text{at} \quad t = 0.$$

As already noted, the solution to the full surface-source problem is self-similar and the solution to this reduced problem is thus of the form $s_0^* = s_0^*(x^*/t^{\frac{1}{2}})$.

## 3. The implant problem

### 3.1. Formulation and initial transient

We now consider the solution to (1) subject to (3) and non-dimensionalise by writing

$$\overline{s} = s/i_m,\ \overline{i} = i/i_m,\ \overline{v} = v/v^*,\ \overline{t} = D_i t/X^2,\ \overline{x} = x/X,\ \overline{F} = F/i_m,$$

where $X$ is a characteristic length scale of the initial distribution $F(x)$. We then obtain the non-dimensional problem (dropping overbars)

$$\varepsilon\mu\frac{\partial s}{\partial t} = -\varepsilon s + iv, \qquad \frac{\partial}{\partial t}(\omega s + v) = \beta\frac{\partial^2 v}{\partial x^2}, \qquad \frac{\partial}{\partial t}(s + i) = \frac{\partial^2 i}{\partial x^2},$$
$$\frac{\partial i}{\partial x} = 0,\ v = 1 \quad \text{on} \quad x = 0; \qquad \frac{\partial i}{\partial x} \to 0,\ \frac{\partial v}{\partial x} \to 0 \quad \text{as} \quad x \to +\infty, \tag{30}$$
$$s = 0,\ i = F(x),\ v = 1 \quad \text{at} \quad t = 0,$$

where

$$\mu = D_i/(k_{dL}X^2), \quad \varepsilon = k_{dL}/(k_{dR}v^*), \quad \beta = D_v/D_i, \quad \omega = i_m/v^*$$

and

$$\max_{x\geq 0} F(x) = 1.$$

Before we begin our analysis of (30), it is worth noting two integrals of the above system which are constant in time. An elementary calculation shows that for all $t$

$$\int_0^\infty (i + s - F(x))\,\mathrm{d}x = 0, \qquad \int_0^\infty x(v + \omega s - 1)\,\mathrm{d}x = 0, \tag{31}$$

where $(31)_1$ is simply a statement of conservation of impurity.

We note from (4) that $\omega > 1$ (for $\omega < 1$ no moving boundaries arise) and we shall again take the limit $\mu \to 0$ followed by $\varepsilon \to 0$. We note, however, that in this case the assumption that $\mu \ll 1$ in fact has little bearing on the rest of the analysis. There are two time scales to consider. The first is an initial transient with $\bar{t} = O(1)$, where $t = \varepsilon\mu\bar{t}$, on which negligible diffusion occurs; the leading-order balance is

$$\frac{\partial s_0}{\partial \bar{t}} = i_0 v_0, \qquad \frac{\partial}{\partial \bar{t}}(\omega s_0 + v_0) = 0, \qquad \frac{\partial}{\partial \bar{t}}(s_0 + i_0) = 0,$$

with solution

$$s_0 = \frac{(1 - \exp((1 - \omega F(x))\bar{t}))F(x)}{\omega F(x) - \exp((1 - \omega F(x))\bar{t})}, \; v_0 = 1 - \omega s_0, \; i_0 = F(x) - s_0. \tag{32}$$

For given $x$, the behaviour of these solutions as $\bar{t} \to +\infty$ depends on whether $\omega F < 1$ or $\omega F > 1$. Wherever $\omega F < 1$, the initial concentration of interstitials is less than the equilibrium vacancy concentration, so that vacancies remain after these interstitials occupy substitutional sites. From (32) we then have

$$\omega F < 1 \quad s_0 \to F, \; v_0 \to 1 - \omega F, \; i_0 \to 0 \quad \text{as} \quad \bar{t} \to +\infty.$$

However, where $\omega F > 1$, the vacancies are all occupied before the impurity can all become substitutional. From (32) we have

$$\omega F < 1 \quad s_0 \to 1/\omega, \; v_0 \to 0, i_0 \to F - 1/\omega \quad \text{as} \quad \bar{t} \to +\infty.$$

For $t = O(1)$ the domain thus splits into distinct regions in which either $v = O(1), i \ll 1$ or $i = O(1), v \ll 1$. These regions are separated by moving boundaries, with narrow transition layers describing the behaviour close to such interfaces.

### 3.2. The moving-boundary problem: formulation

We now discuss the behaviour for $t = O(1)$. In regions in which $i \ll 1$, which we shall denote as $v$ regions, we write

$$s \sim s_0(x,t), \; v \sim v_0(x,t), \; i \sim \varepsilon\tilde{i}_0(x,t)$$

to yield

$$s_0 = \tilde{i}_0 v_0, \qquad \frac{\partial s_0}{\partial t} = 0, \qquad \frac{\partial v_0}{\partial t} = \beta \frac{\partial^2 v_0}{\partial x^2}, \tag{33}$$

whereas in regions in which $v \ll 1$ ($i$ regions) we write

$$s \sim s_0(x,t), \; v \sim \varepsilon\tilde{v}_0(x,t), \; i \sim i_0(x,t)$$

to give

$$s_0 = \tilde{i}_0 v_0, \qquad \frac{\partial s_0}{\partial t} = 0, \qquad \frac{\partial i_0}{\partial t} = \frac{\partial^2 i_0}{\partial x^2}, \tag{34}$$

Even though $\partial s_0/\partial t = 0$ in both cases, we cannot conclude that $s_0$ is fixed for all $t$. In the transition layers at the moving boundaries $s$ varies rapidly with $t$, so that $s_0$ is modified wherever these interfaces move.

We now determine the behaviour in these transition layers and therefore obtain conditions on (33) and (34) at the moving boundaries. We again define $z$ by $x = q(t;\varepsilon) + \varepsilon^{\frac{1}{2}} z$ and write

$$q \sim q_0(t),\ s \sim s_0^\dagger(z,t),\ v \sim \varepsilon^{\frac{1}{2}} v_0^\dagger(z,t),\ i \sim \varepsilon^{\frac{1}{2}} i_0^\dagger(z,t).$$

Assuming that $\mu \ll \varepsilon^{\frac{1}{2}}$, we then recover the system (19). Defining

$$S^-(t) \equiv \lim_{z\to-\infty} s_0^\dagger, S^+(t) \equiv \lim_{z\to+\infty} s_0^\dagger$$

and, treating the case in which the region to the right of $x = q$ is an $i$ region and that to the left a $v$ region (the results for the reverse case follow in an obvious fashion), we observe that matching implies

$$-\omega \dot{q}_0 (s_0^\dagger - S^+) \ = \ \beta \frac{\partial v_0^\dagger}{\partial z}, \qquad -\dot{q}_0 (s_0^\dagger - S^+) = \frac{\partial i_0^\dagger}{\partial z}. \tag{35}$$

The solution to (35) may be written in terms of parabolic cylinder functions:
(i) $S^- > S^+$, which requires $\dot{q}_0 > 0$.

$$v_0^\dagger = \left(\frac{\omega}{\beta}(S^- - S^+)\right)^{\frac{1}{2}} D_{\nu+1}(\zeta)/D_\nu(\zeta),$$

$$i_0^\dagger = S^- D_{\nu-1}(\zeta)/\left(\frac{\omega}{\beta}(S^- - S^+)\right)^{\frac{1}{2}} D_\nu(\zeta),$$

with $\quad s_0^\dagger = i_0^\dagger v_0^\dagger, \nu = -S^-/(S^- - S^+) \quad$ and $\quad \zeta = -\left(\frac{\omega}{\beta}(S^- - S^+)\right)^{\frac{1}{2}} \dot{q}_0 z.$

(ii) $S^- < S^+$, which requires $\dot{q}_0 < 0$.

$$v_0^\dagger = S^+ D_{\nu-1}(\zeta)/\left(\frac{\beta}{\omega}(S^+ - S^-)\right)^{\frac{1}{2}} D_\nu(\zeta),$$

$$i_0^\dagger = \left(\frac{\beta}{\omega}(S^+ - S^-)\right)^{\frac{1}{2}} D_{\nu+1}(\zeta)/D_\nu(\zeta),$$

with $\quad s_0^\dagger = i_0^\dagger v_0^\dagger, \nu = -S^+/(S^+ - S^-) \quad$ and $\quad \zeta = -\left(\frac{\omega}{\beta}(S^+ - S^-)\right)^{\frac{1}{2}} \dot{q}_0 z.$

The profiles in the transition layers thus depend on the direction in which the interface is moving.

We are now in a position to write down the moving-boundary problem. For simplicity, we shall mainly discuss the case in which $F$ is monotonic increasing and bounded, being such that (after the initial transient) there is a single vacancy region adjacent to the surface. We note that this implies that $F(+\infty) = 1 > 1/\omega$. An implant of this form is illustrated in Figure 2. In practice, implant concentrations will decrease back to zero further into the semiconductor and we shall mention the behaviour of such cases later. In Figure 3 we illustrate the vacancy, interstitial and substitutional profiles as well as the moving boundary and transition layer, by means of a numerical solution of (30). By matching with (35) we find that

$$\begin{aligned} \dot{q}_0((s_0)^- - (s_0)^+) \ &= \ \left(\frac{\partial i_0}{\partial x}\right)^+, \\ \dot{q}_0((s_0)^- - (s_0)^+) \ &= \ -\beta \left(\frac{\partial v_0}{\partial x}\right)^- . \end{aligned} \tag{36}$$

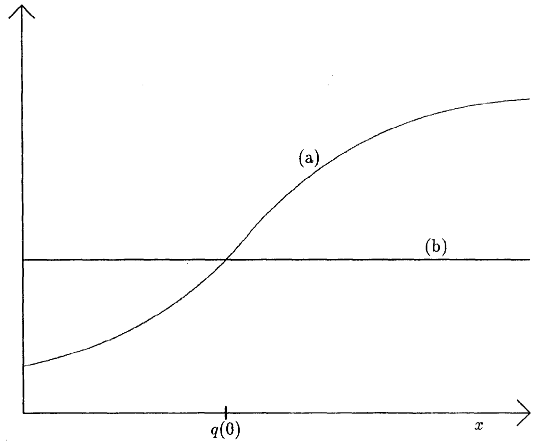


*Figure 2.*

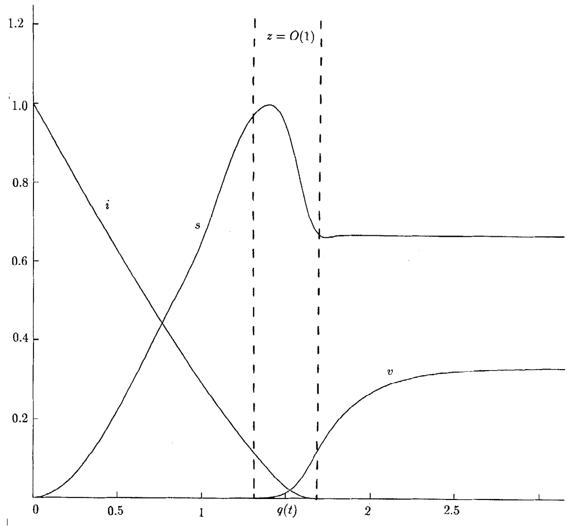


*Figure 3.*

We now have the following moving-boundary problem for $i_0$ and $v_0$

$$\frac{\partial v_0}{\partial t} = \beta\,\frac{\partial^2 v_0}{\partial x^2}, \tag{37}$$

$$v_0 = 1 - \omega F(x) \quad \text{at} \quad t = 0, \qquad v_0 = 1 \quad \text{on} \quad x = 0, \qquad v_0 = 0 \quad \text{on} \quad x = q_0(t),$$

for $x < q_0(t)$, and

$$\begin{aligned} &\frac{\partial i_0}{\partial t} = \frac{\partial^2 i_0}{\partial x^2}\,, \\ &i_0 = F(x) - 1/\omega \quad \text{at} \quad t = 0, \qquad i_0 = 0 \quad \text{on} \quad x = q_0(t), \\ &i_0 \to 1 - 1/\omega \quad \text{as} \quad x \to +\infty, \end{aligned} \tag{38}$$

for $x > q_0(t)$. From (36) we see that

$$\beta\left(\frac{\partial v_0}{\partial x}\right)^{-} = -\omega\left(\frac{\partial i_0}{\partial x}\right)^{+}. \tag{39}$$

Equations (37), (38) and (39) form the complete problem for $i_0, v_0$ and $q_0$.

We note that we can thus solve for $i_0, v_0$ and $q_0$ independently of $s_0$, which is determined from

$$\begin{aligned}
&\frac{\partial s_0}{\partial t} = 0 \quad \text{for} \quad x < q_0(t) \quad \text{and} \quad x > q_0(t), \\
&s_0 = F(x) \quad \text{for} \quad x < q_0(0) \quad \text{and} \quad s_0 = 1/\omega \quad \text{for} \quad x > q_0(0) \quad \text{at} \quad t = 0, \qquad (40) \\
&(s_0)^+ = (s_0)^- - \frac{1}{\dot{q}_0}\left(\frac{\partial i_0}{\partial x}\right)^+,
\end{aligned}$$

the final condition of which shows that the substitutional profile is not constant in time. The outer substitutional profile thus evolves in a curious way, the only point for which $\partial s_0/\partial t$ is non-zero being $x = q_0(t)$. Hence the substitutional concentration at a point only changes if $q_0(t)$ visits that point. We also note that the outer substitutional concentration $s_0$ is discontinuous at the boundary, with the jump in the concentration being proportional to the slope of the interstitials at the right of the front (or, from (39), the slope of the vacancies at the left of the front). Since $(\partial i_0/\partial x)^+$ is positive, $s_0$ is larger at values of $x$ just visited by $q_0(t)$ than at values about to be visited, whatever the sign of $\dot{q}_0$, which is to be expected. We now discuss such behaviour in slightly more detail and then consider some illustrative special cases.

(i) $\dot{q} > 0$.

If $\dot{q} > 0$ for all $t$, then clearly $(s_0)^+ \equiv 1/\omega$ and from $(40)_2$ it follows that $(s_0)^- > (s_0)^+$ (the condition that $\dot{q}_0 > 0$ for $(s_0)^- > (s_0)^+$ is also required by (35), as noted above). The substitutional profile has the form

$$s_0(x,t) = \begin{cases} F(x) & \text{for} \quad 0 < x < q_0(0), \\ 1/\omega + \dfrac{1}{\dot{q}_0}\left(\dfrac{\partial i_0}{\partial x}\right)(x, q_0^{-1}(x)) & \text{for} \quad q_0(0) < x < q_0(t), \\ 1/\omega & \text{for} \quad x > q_0(t), \end{cases} \qquad (41)$$

where $t = q_0^{-1}(x)$ is the time at which the moving boundary crosses the point $x$.

(ii) $\dot{q}_0 < 0$.

We now have $(s_0)^- = F(q_0)$ and $(s_0)^+ > (s_0)^-$. The substitutional profile is given by

$$s_0(x,t) = \begin{cases} F(x) & \text{for} \quad 0 < x < q_0(t), \\ F(x) - \dfrac{1}{\dot{q}_0}\left(\dfrac{\partial i_0}{\partial x}\right)(x, q_0^{-1}(x)) & \text{for} \quad q_0(t) < x < q_0(0), \\ 1/\omega & \text{for} \quad x > q_0(0), \end{cases} \qquad (42)$$

It is not, however, possible for $\dot{q}_0$ to be negative for all $t$. The boundary condition $v_0 = 1$ on $x = 0$ implies that eventually $\dot{q}_0 > 0$ and that the solutions for $i_0, v_0$ and $q_0$ converge to the similarity solution of Section 3.3.1 as $t \to +\infty$. Under such circumstances there will be values of $x$ which are visited by $q_0(t)$ more than once and the resulting profile for $s_0$ will typically be rather complex.

A simple illustration of such behaviour, with $\dot{q}_0 < 0$ for small time and $\dot{q}_0 > 0$ for large time, can be given by considering the further limit $\beta \to 0$. For sufficiently small $t$ we have

$\dot{q}_0 < 0$ and the $v$ region subdivides into three with

$$\begin{array}{ll} v_0 \sim 1 - \omega F(x) & \text{as } \beta \to 0 \text{ with } x = O(1), 0 < x < q_0, \\ v_0 \sim (1 - \omega F(q_0))(1 - \exp(-\dot{q}_0(x - q_0)/\beta)) & \text{as } \beta \to 0 \text{ with } x = q_0(t) + O(\beta), \end{array}$$

together with a boundary layer $x = O(\beta^{\frac{1}{2}})$ at the surface. The $i$ region then decouples, with (39) implying that as $\beta \to 0$

$$\omega \frac{\partial i_0}{\partial x} \sim -\dot{q}_0(1 - \omega F(q_0)) \quad \text{on} \quad x = q_0(t), \qquad s_0 \sim 1/\omega \quad \text{for} \quad x > q_0(t). \tag{43}$$

At some finite value of $t$ the moving boundary $x = q_0$ reaches the surface $x = 0$ (or, more precisely, $q_0$ becomes of $O(\beta)$) and then on the much slower time scale $T = \beta^2 t$ moves back into the semiconductor, with as $\beta \to 0$

$$\begin{array}{l} v_0 \sim 1 - x/q_0(T) \\ i_0 \sim (1 - 1/\omega)\,\mathrm{erf}(X/2\sqrt{T}) \quad \text{for} \quad X = O(1), \quad \text{where} \quad X = \beta x, \end{array}$$

for $T = O(1)$, and with

$$q_0 \sim \sqrt{\pi T}/(\omega - 1),$$

so that $\dot{q}_0 > 0$.

## 3.3. THE MOVING-BOUNDARY PROBLEM: SIMILARITY SOLUTIONS

### 3.3.1. $F(x) \equiv 1$

In this section we shall give two simple similarity solutions to the moving-boundary problem, the first corresponding to the special case in which $F(x) \equiv 1$ in (37)–(39). In both cases the similarity variable is $\eta = x/\sqrt{t}$.

We write $q_0(t) = \alpha\sqrt{t}$ and it is thus clear that $\dot{q}_0 > 0$. The solution is then given by

$$s_0 = \frac{1}{\omega} + \frac{2(\omega - 1)}{\sqrt{\pi}\alpha\omega} \frac{\exp(-\alpha^2/4)}{\mathrm{erfc}(\alpha/2)}, \qquad v_0 = 1 - \frac{\mathrm{erfc}(x/2\sqrt{\beta t})}{\mathrm{erf}(\alpha/2\sqrt{\beta})},$$

for $x < \alpha\sqrt{t}$ and

$$s_0 = 1/\omega, \qquad i_0 = (1 - 1/\omega)(1 - \mathrm{erfc}(x/2\sqrt{t})/\,\mathrm{erfc}(\alpha/2)),$$

for $x > \alpha\sqrt{t}$. The constant $\alpha$ is determined by

$$(\omega - 1)\exp(\alpha^2/4\beta)\,\mathrm{erf}(\alpha/2\sqrt{\beta}) = \sqrt{\beta}\exp(\alpha^2/4)\,\mathrm{erfc}(\alpha/2).$$

As already noted, this solution describes the behaviour in the limit $t \to +\infty$ for more general initial conditions.

### 3.3.2. *An infinite-domain problem*

We now consider a set of boundary and initial conditions which differ from the semi-infinite-domain problems discussed above. The similarity solutions which result have a number of interesting features and the results are instructive with respect to the two-dimensional problem discussed later. Specifically, we replace the boundary and initial conditions in (5) by

$$v \to 1,\ i \to 0 \quad \text{as} \quad x \to -\infty, \qquad v \to 1,\ i \to 1 \quad \text{as} \quad x \to +\infty,$$
$$s = 0,\ v = 1,\ i = F(x) \quad \text{at} \quad t = 0,$$

and we take $F(x)$ to be

$$F(x) = \begin{cases} 0 & \text{for} \quad x < 0, \\ 1 & \text{for} \quad x > 0. \end{cases} \tag{44}$$

and again we assume $\omega > 1$. Following the initial transient, we then have for $t = O(1)$ the following moving-boundary problem. For $-\infty < x < q_0(t)$ there is a $v$ region with $i \ll 1$ and

$$\frac{\partial s_0}{\partial t} = 0, \qquad \frac{\partial v_0}{\partial t} = \beta \frac{\partial^2 v_0}{\partial x^2}\,,$$
$$v_0 \to 1 \quad \text{as} \quad x \to -\infty, \qquad v_0 = 0 \quad \text{on} \quad x = q_0(t), \tag{45}$$

while in $q_0(t) < x < +\infty$ we have an $i$ region with $v \ll 1$ and

$$\frac{\partial s_0}{\partial t} = 0, \qquad \frac{\partial i_0}{\partial t} = \frac{\partial^2 i_0}{\partial x^2}\,,$$
$$i_0 = 0 \quad \text{on} \quad x = q_0(t), \qquad i_0 \to 1 - 1/\omega \quad \text{as} \quad x \to +\infty, \tag{46}$$

The problem is completed by the moving-boundary condition (39). Writing $q_0(t) = \varphi\sqrt{t}$, we then obtain the following similarity solution

$$v_0 = \frac{\operatorname{erf}(\varphi/2\sqrt{\beta}) - \operatorname{erf}(x/2\sqrt{\beta t})}{\operatorname{erfc}(-\varphi/2\sqrt{\beta})}\,, \quad x < \varphi\sqrt{t}, \tag{47}$$

and

$$i_0 = (1 - 1/\omega)\,\frac{\operatorname{erf}(x/2\sqrt{t}) - \operatorname{erf}(\varphi/2)}{\operatorname{erfc}(\varphi/2)}\,, \quad x > \varphi\sqrt{t}\,, \tag{48}$$

with $\varphi$ determined by

$$(\omega - 1)\exp(\varphi^2/4\beta)\operatorname{erfc}(-\varphi/2\sqrt{\beta}) = \sqrt{\beta}\exp(\varphi^2/4)\operatorname{erfc}(\varphi/2)\,. \tag{49}$$

The substitutional concentrations behind and ahead of the front are again related by $(40)_2$ and here we have

$$(s_0)^+ = (s_0)^- - \frac{2(1 - 1/\omega)}{\sqrt{\pi}\varphi}\,\frac{\exp(-\varphi^2/4)}{\operatorname{erfc}(\varphi/2)}\,.$$

From (49) we see that $\varphi = 0$ for $\beta = \beta_c$, where $\beta_c = (\omega - 1)^2$, so the boundary is stationary when the parameters $\beta$ and $\omega$ satisfy this relationship. It is easily shown that for $\beta < \beta_c$ we have $\varphi < 0$, so the front moves to the left, while for $\beta > \beta_c$ we have $\varphi > 0$, the front moving to the right.

If $\varphi > 0$, then $(s_0)^+ = 1/\omega$ and

$$(s_0)^- = \frac{1}{\omega} + \frac{2(1 - 1/\omega)}{\sqrt{\pi}\varphi}\,\frac{\exp(-\varphi^2/4)}{\operatorname{erfc}(\varphi/2)}\,.$$

We then have

$$s(x,t) = \begin{cases} 0 & \text{for} \quad x < 0, \\ (s_0)^- & \text{for} \quad 0 < x < \varphi\sqrt{t}, \\ 1/\omega & \text{for} \quad x > \varphi\sqrt{t}. \end{cases} \tag{50}$$

If $\varphi < 0$ then $(s_0)^- = 0$ and

$$(s_0)^+ = -\frac{2(1-1/\omega)}{\sqrt{\pi}\varphi} \frac{\exp(-\varphi^2/4)}{\text{erfc}(\varphi/2)}$$

and

$$s(x,t) = \begin{cases} 0 & \text{for} \quad 0 < x < \varphi\sqrt{t}, \\ (s_0)^+ & \text{for} \quad \varphi\sqrt{t} < x < 0, \\ 1/\omega & \text{for} \quad x > 0. \end{cases} \tag{51}$$

It follows from (49) that

$$\varphi \sim \frac{\sqrt{\pi}}{2\omega(\omega-1)}(\beta - \beta_c) \quad \text{as} \quad \beta \to \beta_c.$$

Letting $\beta \to \beta_c^+$, we thus have that

$$(s_0)^- \sim \frac{4(\omega-1)^2}{\pi(\beta-\beta_c)},$$

while as $\beta \to \beta_c^-$ we have

$$(s_0)^+ \sim \frac{4(\omega-1)^2}{\pi(\beta_c-\beta)}.$$

Hence, in the limit $\beta \to \beta_c$, the substitutional concentration blows up at the front like $1/(\beta-\beta_c)$. If the front moves slowly, many interstitials are able to become substitutional in the neighbourhood of the front, and there is a build-up of substitutionals behind the front whose concentration is inversely proportional to the front speed. A more detailed analysis of this behaviour requires consideration of the case $\beta = \beta_c + \varepsilon^{\frac{1}{3}}\gamma$, where $\gamma = O(1)$, for which the interior-layer behaviour is no longer given by (35). In this case the outer solutions are

$$x < 0 : v_0 \ = \ \text{erf}(-x/2\sqrt{\beta_c t}),$$
$$x > 0 : i_0 \ = \ (1-1/\omega)\,\text{erf}(x/2\sqrt{t}),$$

while the inner scalings are (*cf.* Section 2.4)

$$x = \varepsilon^{\frac{1}{3}}x^*,\ s \sim \varepsilon^{-\frac{1}{3}}s_0^*(x^*,t),\ v \sim \varepsilon^{\frac{1}{3}}v_0^*(x^*,t),\ i \sim \varepsilon^{\frac{1}{3}}i_0^*(x^*,t). \tag{52}$$

We then obtain

$$\beta_c v_0^* - \omega i_0^* = -(\omega-1)x^*/\sqrt{\pi t} + \gamma/2\omega$$

(higher-order matching is required in order to determine the second term on the right-hand side of this expression) and, using $s_0^* = i_0^* v_0^*$, we find that $s_0^*$ satisfies the somewhat unusual nonlinear diffusion problem

$$\frac{\partial s_0^*}{\partial t} = \frac{1}{2\omega}\frac{\partial^2}{\partial x^{*2}}\left(\left(\left(\frac{\omega-1}{\sqrt{\pi t}}x^* - \frac{\gamma}{2\omega}\right)^2 + 4\omega(\omega-1)^2 s_0^*\right)^{\frac{1}{2}}\right),$$
$$s_0^* \to 0 \quad \text{as} \quad |x^*| \to \infty, \qquad s_0^* = 0 \quad \text{at} \quad t = 0, \tag{53}$$

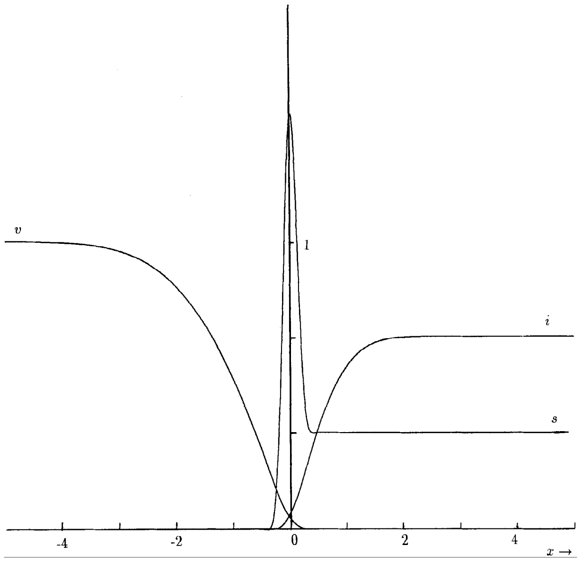


*Figure 4.*

with

$$\int_{-\infty}^{\infty} s_0^* \, \mathrm{d}x^* = 2(\omega - 1)\sqrt{t}/\omega\sqrt{\pi}, \quad \int_{-\infty}^{\infty} x^* s_0^* \, \mathrm{d}x^* = \gamma t / 2\omega^2.$$

The scaling $s = O(\varepsilon^{-\frac{1}{3}})$ in (52) indicates the unusual nature of the substitutional profile, with a sharp peak close to $x = 0$. A numerical solution for $\beta = \beta_c$ is given in Figure 4.

### 3.4. More realistic implants

The special cases already discussed give some indication of the variety of possible behaviours which can occur. Here we briefly consider the more realistic case in which the implant profile $F(x)$ in (30) decays to zero as $x \to +\infty$ and there are two $v$ regions ($0 < x < q_0(t)$ and $Q_0(t) < x < \infty$, say). We note that, even if $F(x)$ is such that there is no $v$ region near $x = 0$ at $t = 0$, there will be one for $t > 0$ because of the surface-boundary condition on $v$, and one $i$ region ($q_0(t) < x < Q_0(t)$). Since the $i$ region contains at $t = 0$ only a finite number of interstitials, the moving boundaries $q_0$ and $Q_0$ will meet at some finite time, at leading order the interstitials all having become substitutional. For times greater than this we have $i \ll 1$ for all $x$ and at leading order for $t = O(1)$ we have simply

$$\frac{\partial v_0}{\partial t} = \beta \frac{\partial^2 v_0}{\partial x^2}, \qquad \frac{\partial s_0}{\partial t} = 0, \tag{54}$$

without moving boundaries present. The substitutionals then redistribute on the much longer time scale $\tau = O(1)$, where $\tau = \varepsilon t$, with

$$v_0 = 1, \qquad \frac{\partial s_0}{\partial \tau} = \frac{\partial^2 s_0}{\partial x^2}. \tag{55}$$

Our remaining comments will concern the further limit $\beta \to 0$, which is again instructive in this context. Taking the limits $\varepsilon \to 0$ and $\beta \to 0$, we obtain at leading order the moving-boundary problem (*cf.* (43))

$$
\begin{aligned}
&\frac{\partial i_0}{\partial t} = \frac{\partial^2 i_0}{\partial x^2} && \text{for} \quad q_0(t) < x < Q_0(t), \\
&i_0 = 0, \omega \frac{\partial i_0}{\partial x} = -\dot{q}_0(1 - \omega F(q_0)) && \text{at} \quad x = q_0(t)\,, \\
&i_0 = 0, \omega \frac{\partial i_0}{\partial x} = -\dot{Q}_0(1 - \omega F(Q_0)) && \text{at} \quad x = Q_0(t)\,, \\
&i_0 = F(x) - 1/\omega \quad \text{for} \quad q_0(0) < x < Q_0(0) && \text{at} \quad t = 0\,,
\end{aligned}
\tag{56}
$$

with $\dot{q}_0 < 0, \dot{Q}_0 > 0$. This formulation holds as long as $q_0 > 0$. If $q_0$ reaches zero, the conditions on $x = q_0(t)$ are replaced by

$$
i_0 = 0 \quad \text{at} \quad x = 0. \tag{57}
$$

It should again be stressed that in the limit $\varepsilon \to 0$ with $\beta = O(1)$, $q_0$ remains positive. However, taking the limits $\varepsilon \to 0$ followed by $\beta \to 0$, we find that $q_0$ may become of $O(\beta)$ in finite time, in which case the condition (57) becomes appropriate. When $q_0 = O(\beta)$, it follows from (40) that $s_0$ becomes of $O(1/\beta)$ in a region of thickness $O(\beta)$, indicating that substitutional concentrations close to the surface become very high; this type of, apparently, uphill diffusion near the surface also arises in other contexts.

While the conditions in (56) remain valid (*i.e.* while $q_0 > 0$), it is readily shown that

$$
\int_{q_0(t)}^{Q_0(t)} (i_0 + 1/\omega - F(x))\,\mathrm{d}x = \int_{q_0(t)}^{Q_0(t)} x(i_0 + 1/\omega - F(x))\,\mathrm{d}x = 0\,, \tag{58}
$$

while, if (57) becomes appropriate, we have

$$
\int_0^{Q_0(t)} x(i_0 + 1/\omega - F(x))\,\mathrm{d}x = 0\,. \tag{59}
$$

The significance of these expressions is the following. As $t \to \infty$, it is found that $i_0$ decays to zero exponentially fast and $q_0(t)$ and $Q_0(t)$ approach constant values $q_0(\infty)$ and $Q_0(\infty)$. These values can be calculated exactly from (58) and (59), whereby we have

$$
q_0(\infty) > 0, \quad \int_{q_0(\infty)}^{Q_0(\infty)} (1/\omega - F(x))\,\mathrm{d}x = \int_{q_0(\infty)}^{Q_0(\infty)} x(1/\omega - F(x))\,\mathrm{d}x = 0
$$

or

$$
q_0(\infty) = 0, \ \int_0^{Q_0(\infty)} x(1/\omega - F(x))\,\mathrm{d}x = 0\,.
$$

On the longer time scale $T = O(1)$, with $T = \beta t$, we have (*cf.* (54))

$$
\begin{aligned}
&\frac{\partial v_0}{\partial T} = \frac{\partial^2 v_0}{\partial x^2}\,, \\
&v_0 = 1 \quad \text{at} \quad x = 0, \qquad v_0 \to 1 \quad \text{as} \quad x \to +\infty, \\
&v_0 = 0, \ 0 < x < Q_0(\infty) \quad \text{at} \qquad T = 0, \\
&v_0 = 1 - \omega F(x), \ Q_0(\infty) < x < \infty \quad \text{at} \quad T = 0,
\end{aligned}
$$

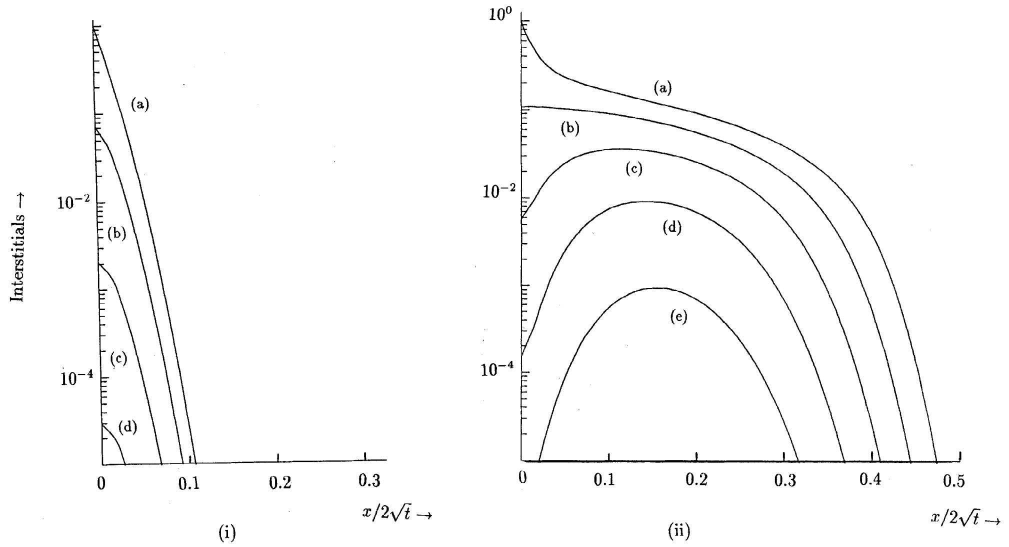


*Figure 5.*

where there are no moving boundaries and for brevity we shall henceforth treat only the case $q_0(\infty) = 0$. For $x = O(1)$ we then have

$$s_0 = 1/\omega,\ 0 < x < Q_0(\infty); \qquad s_0 = F(x),\ Q_0(\infty) < x < \infty, \tag{60}$$

with, as already noted, a region of very high substitutional concentration close to $x = 0$. The substitutional impurity thus adopts a highly distinctive profile, including a region of almost constant concentration, given in dimensional terms by $s \sim v^*$ (the equilibrium vacancy concentration). Finally, on the even longer time scale $\tau = O(1)$ we have (55) subject to

$$s_0 = \left\{\int_0^{Q_0(\infty)} \left(F(x) - \frac{1}{\omega}\right)\, \mathrm{d}x\right\}\delta(x) + \frac{1}{\omega}H(Q_0(\infty) - x)$$
$$+ F(x)H(x - Q_0(\infty)) \quad \text{at} \quad \tau = 0\,,$$
$$\frac{\partial s_0}{\partial x} = 0 \quad \text{at} \quad x = 0\,, \qquad s_0 \to 0 \quad \text{as} \quad x \to +\infty\,,$$

where $H$ is the Heaviside step-function and the initial condition follows from (60), the $\delta$-function representing the impurity located in the narrow high-concentration region near the surface (in which substitutional diffusion commences when $t = O(\beta^2/\varepsilon)$).

## 4. Two-dimensional surface-source problem

### 4.1. Formulation and Boundary Layer

This section is concerned with two-dimensional diffusion under a mask edge. This problem has been discussed under a different limit in Meere *et al.* [5], where it was shown that the dissociative mechanism can produce unusual types of diffused profiles exhibiting a 'bird's beak'. We shall see here that the current limit also leads to some unusual profiles, but of a significantly different type. Such differences are potentially of value in the assessment of diffusion mechanisms and parameter values experimentally.

Figure 5 illustrates results from the numerical solution to the two-dimensional problem (61) by giving interstitial profiles as functions of $x$ for various values of $y$. A particularly noteworthy, and somewhat surprising, feature of these is that for $\omega = 3$ the profiles (c)–(e) exhibit interior maxima beneath the mask; by contrast, for $\omega = 0.75$ the profiles are monotonically decreasing. This type of behaviour will be explained by the asymptotic analysis given below.

The relevant two-dimensional initial-boundary-value problem takes the form

$$
\begin{aligned}
&s = iv, \qquad \frac{\partial}{\partial t}(\omega s + \varepsilon v) = \varepsilon\beta\nabla^2 v, \qquad \frac{\partial}{\partial t}(s + \varepsilon i) = \varepsilon\nabla^2 i,\\
&v = 1, i = 1 \quad \text{on} \quad x = 0,\, y > 0, \qquad v = 1,\, \frac{\partial i}{\partial x} = 0 \quad \text{on} \quad x = 0,\, y < 0,\\
&v \to 1, i \to 0 \quad \text{as}\ x \to +\infty \quad \text{or} \quad y \to -\infty, \qquad\qquad (61)\\
&\frac{\partial v}{\partial y} \to 0,\, \frac{\partial i}{\partial y} \to 0 \quad \text{as} \quad y \to +\infty, \qquad v = 1,\, i = 0 \quad \text{at} \quad t = 0.
\end{aligned}
$$

Here $x = 0$ is again the semiconductor surface, with $y > 0$ representing a window which contains an impurity source and $y < 0$ being covered by a mask which is impermeable to impurity. The behaviour as $y \to +\infty$ is given by the one-dimensional problem of Section 2. A more detailed description is given in [5]. The solution takes the self-similar form

$$s = s(x/t^{\frac{1}{2}}, y/t^{\frac{1}{2}}),\, i = i(x/t^{\frac{1}{2}},\, y/t^{\frac{1}{2}}), v = v(x/t^{\frac{1}{2}}, y/t^{\frac{1}{2}}).$$

A boundary layer occurs near $x = 0$ for $y > 0$ with, as in Section 2.1,

$$x = \varepsilon^{\frac{1}{2}}\widehat{x},\, s \sim \widehat{s}_0(\widehat{x}, t),\, v \sim \widehat{v}_0(\widehat{x}, t),\, i \sim \widehat{i}_0(\widehat{x}, t),$$

the leading-order solution being given by (9)–(11). The results (12)–(13) again describe the matching out of the boundary layer, so we must also distinguish the cases $\beta > \omega$ and $\beta < \omega$ here.

## 4.2. $\beta > \omega$

We again start with the simpler case in which moving boundaries do not arise. In $x = O(1)$, $s$ and $i$ are exponentially small and, writing $v \sim v_0(x, y, t)$, we have

$$
\begin{aligned}
&\frac{\partial v_0}{\partial t} = \beta\left(\frac{\partial^2 v_0}{\partial x^2} + \frac{\partial^2 v_0}{\partial y^2}\right),\\
&v_0 = 1 - \frac{\omega}{\beta} \quad \text{on} \quad x = 0,\, y > 0,\, v_0 = 1 \quad \text{on} \quad x = 0,\, y < 0,\\
&v_0 \to 1 \quad \text{as} \quad x \to +\infty \quad \text{or} \quad y \to -\infty,\, \frac{\partial v_0}{\partial y} \to 0 \quad \text{as} \quad y \to +\infty,\\
&v_0 = 1 \quad \text{at} \quad t = 0,
\end{aligned}
$$

with solution

$$v_0 = 1 - \frac{\omega}{\sqrt{\pi}\beta}\int_{x/2\sqrt{\beta t}}^{\infty} e^{-\mu^2}\left(1 + \text{erf}\left(\frac{y}{x}\,\mu\right)\right) \mathrm{d}\mu. \qquad (62)$$

There is a further inner region close to the mask edge with

$$x = \varepsilon^{\frac{1}{2}}\widehat{x},\; y = \varepsilon^{\frac{1}{2}}\widehat{y},\; s \sim \overline{s}_0(\widehat{x},\widehat{y},t),\; v \sim \overline{v}_0(\widehat{x},\widehat{y},t),\; i \sim \overline{i}_0(\widehat{x},\widehat{y},t), \tag{63}$$

with

$$\begin{aligned}
&\overline{s}_0 = \overline{i}_0\overline{v}_0, \quad \frac{\partial \overline{s}_0}{\partial t} = \nabla^2\overline{i}_0, \quad \nabla^2(\omega\overline{i}_0 - \beta\overline{v}_0) = 0,\\
&\overline{v}_0 = 1,\, \overline{i}_0 = 1 \quad \text{on} \quad \widehat{x} = 0,\, \widehat{y} > 0,\, \overline{v}_0 = 1,\, \frac{\partial \overline{i}_0}{\partial \widehat{x}} = 0 \quad \text{on} \quad \widehat{x} = 0, \widehat{y} < 0,\\
&\frac{\partial \overline{v}_0}{\partial \widehat{y}} \to 0,\, \frac{\partial \overline{i}_0}{\partial \widehat{y}} \to 0 \quad \text{as} \quad \widehat{y} \to +\infty, \qquad (64)\\
&\overline{v}_0 \sim 1 - \frac{\omega}{\pi\beta}\left(\theta + \frac{\pi}{2}\right),\, \overline{i}_0 \to 0 ds \widehat{r} \to +\infty,\, \theta \neq \frac{\pi}{2}\,,\\
&\overline{s}_0 = 0 \quad \text{at} \quad t = 0,
\end{aligned}$$

where $\widehat{x} = \widehat{r}\cos\theta,\; \widehat{y} = \widehat{r} = \sin\theta$.

## 4.3. $\beta < \omega$

### 4.3.1. *The moving-boundary problem*

In $x, y = O(1)$ the following moving-boundary problem may be deduced in a manner similar to those of the previous sections; we denote the moving boundary by $t = \sigma(x, y)$.

<u>$i$ region</u> $(t > \sigma(x,y))$

$$s \sim \varepsilon\tilde{s}_0(x,y,t),\; v \sim \varepsilon\tilde{v}_0(x,y,t),\; i \sim i_0(x,y,t).$$

$$\begin{aligned}
&\frac{\partial i_0}{\partial t} = \frac{\partial^2 i_0}{\partial x^2} + \frac{\partial^2 i_0}{\partial y^2}\,, \qquad (65)\\
&i_0 = 1 - \beta/\omega \quad \text{on} \quad x = 0,\, y > 0,\\
&i_0 \sim (1 - \beta/\omega)(1 - \operatorname{erf}(x/2\sqrt{t})/\operatorname{erf}(\alpha/2)) \quad \text{as} \quad y \to +\infty,\, 0 < x < \alpha\sqrt{t},
\end{aligned}$$

where $\alpha$ is given by (26), with

$$\tilde{s}_0 = i_0\tilde{v}_0, \quad \frac{\partial \tilde{s}_0}{\partial t} = 0\,. \tag{66}$$

<u>$v$ region</u> $(t < \sigma(x,y))$

$v \sim v_0(x,y,t), s$ and $i$ are exponentially small.

$$\begin{aligned}
&\frac{\partial v_0}{\partial t} = \beta\left(\frac{\partial^2 v_0}{\partial x^2} + \frac{\partial^2 v_0}{\partial y^2}\right)\,,\\
&v_0 = 1 \quad \text{on} \quad x = 0,\, y < 0, \qquad (67)\\
&v_0 \to 1 \quad \text{as} \quad x \to +\infty \quad \text{or} \quad y \to -\infty,\\
&v_0 \sim 1 - \operatorname{erfc}(x/2\sqrt{\beta t})/\operatorname{erfc}(\alpha/2\sqrt{\beta}) \quad \text{as} \quad y \to +\infty,\, x > \alpha\sqrt{t}\,.
\end{aligned}$$

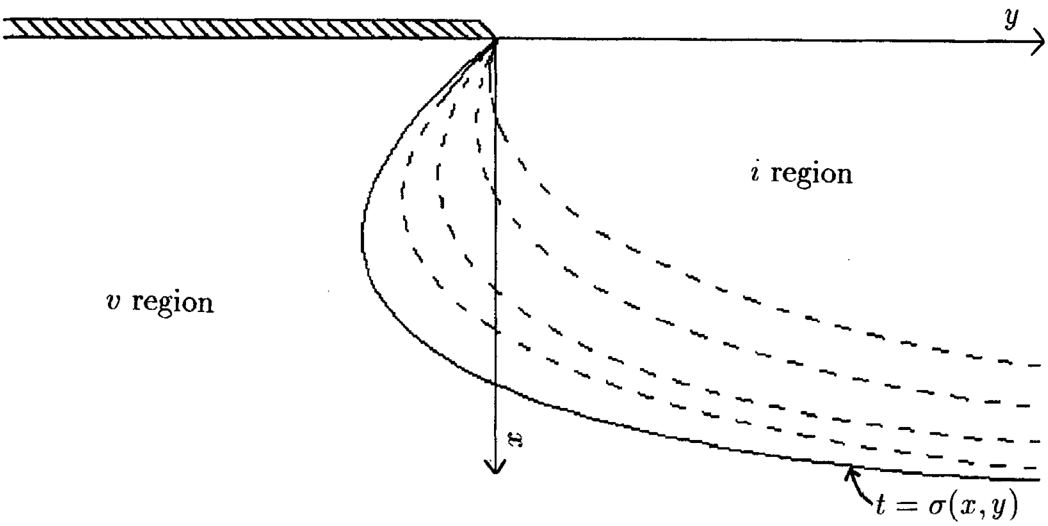


*Figure 6.*

We now use $(\ )^+$ and $(\ )^-$ to denote the limits as the moving boundary is approached from within the $v$ region and the $i$ region, respectively. The moving-boundary conditions which couple (65) and (67) and complete the specification of the moving-boundary problem are then

$$(i_0)^- = 0,\ (v_0)^+ = 0,\ \beta\left(\frac{\partial v_0}{\partial n}\right)^+ = -\omega\left(\frac{\partial i_0}{\partial n}\right)^- \quad \text{on} \quad t = \sigma(x, y), \tag{68}$$

where $\frac{\partial}{\partial n} \equiv \frac{\nabla\sigma}{|\nabla\sigma|} \cdot \nabla$ denotes the outward normal derivative. Finally, we also have

$$(\tilde{s}_0)^- = -(\nabla\sigma \cdot \nabla i_0)^-, \tag{69}$$

which may alternatively be written in the form

$$V_n(\tilde{s}_0)^- = -\left(\frac{\partial i_0}{\partial n}\right)^-, \tag{70}$$

where $V_n = 1/|\nabla\sigma|$ denotes the outward normal velocity of the moving boundary. A schematic of a possible form for the moving boundary is indicated in Figure 6. It should be noted that the moving boundary meets the surface $(x = 0)$ at the edge of the mask $(x = 0, y = 0)$.

Before proceeding to describe the remainder of the asymptotic structure, we first note a reformulation of the moving-boundary problem as a nonlinear diffusion problem and then describe its local behaviour near the mask edge.

If we introduce

$$c = \omega i_0 - \beta v_0,$$

we obtain the fixed-domain problem

$$\frac{\partial}{\partial t}(\Phi(c)) = \nabla^2 c,$$

$$c = \omega - \beta \quad \text{on} \quad x = 0,\ y > 0, \qquad c = -\beta \quad \text{on} \quad x = 0,\ y < 0, \tag{71}$$

$$c \to -\beta \quad \text{as} \quad x \to +\infty \text{ or } y \to -\infty,$$

$$\frac{\partial c}{\partial y} \to 0 \quad \text{as} \quad y \to +\infty, \qquad c = -\beta \quad \text{at} \quad t = 0,$$

where

$$\Phi(c) = \begin{cases} c & c > 0, \\ c/\beta & c < 0, \end{cases}$$

is a piecewise linear function. If (71) is solved, then the moving boundary is given by the concentration contour $c = 0$. In the special case $\beta = 1$, (71) is linear and has solution

$$c = \frac{\omega}{\sqrt{\pi}} \int_{x/2\sqrt{t}}^{\infty} e^{-\mu^2} \left(1 + \text{erf}\left(\frac{y}{x}\,\mu\right)\right)\, \mathrm{d}\mu - 1\,.$$

The local behaviour close to $x = 0$, $y = 0$ will play an important role in the remainder of the analysis. It is readily shown that

$$\beta v_0 - \omega i_0 \sim \beta - \omega(\theta + \pi/2)/\pi + \gamma(t) r \cos\theta \tag{72}$$

as $r \to 0$, where $x = r\cos\theta$, $y = r\sin\theta$ and $\gamma(t) = \gamma_0 t^{-\frac{1}{2}}$, the constant $\gamma_0$ being determined globally. The moving boundary thus takes the form

$$\theta \sim \theta_0 + \pi\gamma_0/(\omega t^{\frac{1}{2}})\, r \sin(\pi\beta/\omega) \quad \text{as} \quad r \to 0\,, \tag{73}$$

where

$$\theta_0 = \pi(\beta/\omega - \tfrac{1}{2})\,.$$

The angle $\theta_0$ at which the moving boundary comes into the mask edge is thus completely determined by the local analysis. We note that, as $\beta/\omega \to 1^-$, the window $\theta = \pi/2$ is approached, whereas for $\beta/\omega \to 0^+$ the mask $\theta = -\pi/2$ is approached. The schematic of Figure 6 corresponds to the case $\beta < 2\omega$ in which the moving boundary bends underneath the mask.

Using self-similarity, we deduce from (66) that

$$\tilde{s}_0 = \tilde{s}_0(\theta)\,,$$

and, using (69) and (73), we may show

$$\tilde{s}_0 \sim 2\pi\gamma_0^2 \sin^2(\pi\beta/\omega)/\{\omega^2(\theta - \theta_0)^3\} \quad \text{as} \quad \theta \to \theta_0^+\,. \tag{74}$$

This 'pile-up' of substitutionals just behind the moving boundary is a consequence of the velocity of the boundary tending to zero as $r \to 0$ (*cf.* Section 3.3.2). We have

$$V_n \sim \pi \sin(\pi\beta/\omega)\gamma_0 r^2/(2\omega t^{\frac{3}{2}}) \quad \text{as } r \to 0\,. \tag{75}$$

The fact that $\tilde{s}_0$ becomes unbounded $\theta \to \theta_0$ indicates the need for an additional region close to $\theta = \theta_0$, which we discuss next.

#### 4.3.2. *Other regions*

There are three regions which we have not described so far. The transition layer located about the moving boundary is, away from the mask edge, one-dimensional at leading order and is thus again of the form (21)–(23). The remaining two regions need to be discussed in more detail. Both are close to the mask edge and the first relates to the substitutional pile-up just referred to, the relevant scalings being

$$\theta = \theta_0 + \varepsilon^{\frac{1}{5}}\phi,\ r = \varepsilon^{\frac{1}{5}}r^* \quad \text{with}$$

$$s \sim \varepsilon^{\frac{2}{5}} s_0^*(r^*, \phi, t),\ v \sim \varepsilon^{\frac{1}{5}} v_0^*(r^*, \phi, t),\ i \sim \varepsilon^{\frac{1}{5}} i_0^*(r^*, \phi, t)$$

and we have

$$s_0^* = i_0^* v_0^*, \quad \omega\frac{\partial s_0^*}{\partial t} = \frac{\beta}{r^{*2}}\frac{\partial^2 v_0^*}{\partial \phi^2}, \quad \frac{\partial s_0^*}{\partial t} = \frac{1}{r^{*2}}\frac{\partial^2 i_0^*}{\partial \phi^2}.$$

By appropriate matching (including at $O(\varepsilon^{\frac{1}{5}})$ – we omit details) we then find that

$$\beta v_0^* - \omega i_0^* = -\omega\phi/\pi + \gamma_0 r^* \sin(\pi\beta/\omega)/t^{\frac{1}{2}},$$

so we have

$$i_0^* = \frac{1}{2\omega}\left\{\left(\left(\frac{\omega}{\pi}\phi - \frac{\gamma_0 r^*}{t^{\frac{1}{2}}}\sin(\pi\beta/\omega)\right)^2 + 4\omega\beta s_0^*\right)^{\frac{1}{2}} + \frac{\omega}{\pi}\phi - \frac{\gamma_0 r^*}{t^{\frac{1}{2}}}\sin(\pi\beta/\omega)\right\},$$

$$v_0^* = \frac{1}{2\beta}\left\{\left(\left(\frac{\omega}{\pi}\phi - \frac{\gamma_0 r^*}{t^{\frac{1}{2}}}\sin(\pi\beta/\omega)\right)^2 + 4\omega\beta s_0^*\right)^{\frac{1}{2}} - \frac{\omega}{\pi}\phi + \frac{\gamma_0 r^*}{t^{\frac{1}{2}}}\sin(\pi\beta/\omega)\right\},$$

together with the nonlinear diffusion problem (*cf.* (53))

$$\frac{\partial s_0^*}{\partial t} = \frac{1}{2\omega r^{*2}}\frac{\partial^2}{\partial \phi^2}\left(\left\{\left(\frac{\omega}{\pi}\phi - \frac{\gamma_0 r^*}{t^{\frac{1}{2}}}\sin(\pi\beta/\omega)\right)^2 + 4\omega\beta s_0^*\right\}^{\frac{1}{2}}\right),$$

$$s_0^* \to 0 \quad \text{as} \quad |\phi| \to \infty, \qquad s_0^* = 0 \quad \text{at} \quad t = 0. \tag{76}$$

The solution to (76) is of the form

$$s_0^* = s_0^*(\phi, t/r^{*2}).$$

We also note the integral results

$$\int_{-\infty}^{\infty} s_0^*\,\mathrm{d}\phi = \frac{t}{\pi r^{*2}}, \qquad \int_{-\infty}^{\infty} \phi s_0^*\,\mathrm{d}\phi = \frac{2\gamma_0 t^{\frac{1}{2}}}{\omega r^*}\sin(\pi\beta/\omega).$$

As $t \to 0$, or equivalently as $r^* \to +\infty$, the solution to (76) takes the form

$$s_0^* \sim t^{\frac{3}{2}} f(z^*)/r^{*3} \quad \text{where} \quad z^* = r^{*\frac{3}{2}}(\phi - \pi\gamma_0 r^* \sin(\pi\beta/\omega)/(\omega t^{\frac{1}{2}}))t^{-\frac{3}{4}}$$

for $z^* = O(1)$, which matches into the transition layer about the moving boundary, and the form

$$s_0^* \sim 2\pi\gamma_0^2 \sin^2(\pi\beta/\omega)/(\omega^2\phi^3) \tag{77}$$

for $\phi = O(r^*/t^{\frac{1}{2}})$ with $t^{\frac{1}{2}}\phi/r^* > \pi\gamma_0 \sin(\pi\beta/\omega)/\omega$, which matches with (74). We note that (77) holds as $\phi \to +\infty$ for all $t > 0$. As $t \to +\infty$, or equivalently as $r^* \to 0$, we have self-similar behaviour of the form

$$s_0^* \sim t^{\frac{2}{3}} g(r^{*\frac{2}{3}}\phi/t^{\frac{1}{3}})/r^{*\frac{4}{3}} \quad \text{for} \quad \phi = O(t^{\frac{1}{3}}/r^{*\frac{2}{3}}) \tag{78}$$

where $g(\eta)$ is an even function of $\eta$, which matches into the final region which we now discuss.

This is the mask-edge region in which the scalings (63) again hold, as does (64), except that the condition as $\widehat{r} \to +\infty$ is replaced by

$$\begin{aligned} \overline{v}_0 \;&\sim\; 1 - \omega(\pi\beta)^{-1}(\theta + \pi/2), \quad \bar{i}_0 \to 0 \quad \text{as} \quad \widehat{r} \to +\infty, \quad -\pi/2 \le \theta < \theta_0\,, \\ \overline{v}_0 \;&\to\; 0, \quad \bar{i}_0 \sim \pi^{-1}(\theta + \pi/2) - \beta/\omega \quad \text{as} \quad \widehat{r} \to +\infty, \quad \theta_0 < \theta < \pi/2\,. \end{aligned} \tag{79}$$

The far-field behaviour of $\overline{s}_0$ is of some interest, $\overline{s}_0$ becoming exponentially small as $\widehat{r} \to +\infty$ for $-\frac{\pi}{2} \le \theta < \theta_0$ and $\theta_0 < \theta < \frac{\pi}{2}$, but only algebraically small for $\theta = \theta_0$, corresponding to matching with (78), with

$$\overline{s}_0 \sim t^{\frac{2}{3}} g(\widehat{r}^{\frac{2}{3}}(\theta - \theta_0)/t^{\frac{1}{3}})/\widehat{r}^{\frac{4}{3}} \quad \text{as} \quad \widehat{r} \to +\infty \quad \text{with} \quad \theta - \theta_0 = O(\widehat{r}^{-\frac{2}{3}})\,. \tag{80}$$

### 4.4. Discussion

In the limit discussed in [5], corresponding in the current notation to $\omega \gg 1$ with $\varepsilon = O(1)$ (less restrictively, the results of [5] also apply for $\varepsilon \ll 1$ provided that $\varepsilon \gg 1/\omega$), impurity contours stretch a substantial distance beneath the mask (in the $-y$ direction), leading to 'bird's-beak' profiles characteristic of greatly enhanced lateral diffusion. By contrast, as Figure 6 indicates, the current limit can lead to contours which curve back towards the edge of the mask. Such results are confirmed by numerical solution of the full model and our main purpose in this section is to give some indication of how these two apparently contradictory types of behaviour (in comparison with linear diffusion, enhanced and reduced impurity concentrations along the bottom of the mask) can arise from the same mechanism.

As indicated in [5], a complete description of the transition between the two cases requires consideration of a number of different relationships between the two small parameters $\varepsilon$ and $1/\omega$, and we shall not pursue the details. However, it is possible to show that the impurity contours at high concentration are qualitatively similar to those of [5] (although the details of the limit problems may differ) whenever $\varepsilon$ and $1/\omega$ are both small, no matter how much smaller the former is than the latter. Therefore by analysing the mask-edge region $\widehat{x}, \widehat{y} = O(1)$ introduced above in the limit $\omega \to \infty$, we will be able to gain understanding of the transition.

We thus consider the behaviour of (64), with the condition as $\widehat{r} \to +\infty$ replaced by (79), in the limit $\omega \to \infty$. The details are rather complicated, the asymptotic structure subdividing into seven regions, a number of which are governed by unusual types of non-local nonlinear diffusion problem. However, for the purposes of this discussion it suffices to describe one of these regions only. It is convenient first to introduce the small parameter $\delta = \beta/\omega$.

The relevant region is a boundary layer with scalings $\widehat{x} = O(1), \widehat{Y} = O(1)$ where $\widehat{Y} = \delta\widehat{y}$, with $\widehat{Y} < 0$, and, writing $\overline{s}_0 \sim \delta S_0(\widehat{x}, \widehat{Y}, t)$ as $\delta \to 0$, we obtain the surface-concentration-dependent nonlinear diffusion problem

$$\frac{\partial S_0}{\partial t} = \frac{1}{2}\frac{\partial^2}{\partial \widehat{x}^2}\left(\left\{\left(\frac{\widehat{x}}{\pi(-\widehat{Y})} + \alpha(\widehat{Y}, t) - 1\right)^2 + 4S_0\right\}^{\frac{1}{2}}\right)\,,$$

$$S_0 = \alpha(\widehat{Y}, t), \; \frac{\partial S_0}{\partial \widehat{x}} = -\frac{\alpha(\widehat{Y}, t)}{\pi(-\widehat{Y})} \quad \text{at} \quad \widehat{x} = 0 \,, \tag{81}$$

$$S_0 \to 0 \quad \text{as} \quad \widehat{x} \to +\infty \,, \qquad S_0 = 0 \quad \text{at} \quad t = 0 \,,$$

which determines the surface concentration $\alpha(\widehat{Y}/t^{\frac{1}{2}})$ as well as $S_0(\widehat{x}/t^{\frac{1}{2}}, \widehat{Y}/t^{\frac{1}{2}})$. For the other variables, we write $\overline{v}_0 \sim V_0(\widehat{x}, \widehat{Y}, t), \overline{i}_0 \sim \delta I_0(\widehat{x}, \widehat{Y}, t)$ as $\delta \to 0$, with

$$S_0 = I_0 V_0, I_0 = V_0 + \pi^{-1}\widehat{x}/(-\widehat{Y}) + \alpha - 1 \,.$$

We note from (81) that

$$\int_0^\infty S_0 \, \mathrm{d}\widehat{x} = t/\pi(-\widehat{Y}), \quad \int_0^\infty \widehat{x} S_0 \, \mathrm{d}\widehat{x} = t \,. \tag{82}$$

The problem (81) has the following asymptotic behaviour.
(i) As $\widehat{Y} \to \mathrm{d}_o$,

$$\alpha \sim t/(\pi^2 \widehat{Y}^2) \,, \quad S_0 \sim t/(\pi^2 \widehat{Y}^2) \, e^{\widehat{e}/\pi \widehat{Y}} \quad \text{for} \quad \widehat{x} = O(-\widehat{Y}) \,. \tag{83}$$

(ii) As $\widehat{Y} \to -\infty$, $\alpha$ becomes exponentially small and

$$S_0 \, t^{\frac{2}{3}}/(-\widehat{Y})^{\frac{4}{3}} \, g((\widehat{x} + \pi\widehat{Y}) t^{-\frac{1}{3}}(-\widehat{Y})^{\frac{1}{3}}) \quad \text{for} \quad \widehat{x} = \pi(-\widehat{Y}) + O(t^{\frac{1}{3}}(-\widehat{Y})^{\frac{1}{3}}) \,. \tag{84}$$

We may therefore deduce the following results, which hold for fixed $t = O(1)$.
(i) For given small $|\widehat{Y}|$, $S_0$ has its maximum at the surface $\widehat{x} = 0$ and decays rapidly into the semiconductor (see (83)). Impurity contours at high concentrations extend much further in the $-\widehat{y}$ direction than in the $\widehat{x}$ direction (*cf.* [5]). Contours with $s = O(1)$ stretch a distance $-\widehat{y} = O(\delta^{-\frac{1}{2}})$ under the mask, though we omit details for this region.
(ii) For given large $|\widehat{Y}|$, $S_0$ is exponentially small on the surface $\widehat{x} = 0$ and has an interior maximum close to the line $\widehat{x} = \pi(-\widehat{Y})$ (see (84)); this location is implicit in the integral relations (82) and corresponds to taking the limit $\delta \to 0$ in $\theta \sim \theta_0$.

It is possible to argue that the region $r^* = O(1)$ discussed in Section 4.3.2, in which $\theta \sim \theta_0$ and where substitutional concentrations are relatively large, represents a rotation of the 'bird's-beak' effect occurring in [5] from immediately beneath the mask (i.e. from $\theta = -\frac{\pi}{2}$) to an angle $\theta = \theta_0$. As $\omega$ increases (and hence $\theta_0$ decreases), the local maximum moves towards the mask, and eventually the limit of [5] is recovered. The local pile-up of substitutional impurity arises from the presence of vacancies made available through surface generation at the mask. In [5] (where $\omega \gg 1, \varepsilon = O(1)$) sufficient impurities diffusing in that surface-generated vacancies are consumed by impurity interstitials right up to the surface, so that the substitutional peak occurs there. In the current case ($\varepsilon \ll 1, \omega = O(1)$) less impurity is present, so that vacancies are able to diffuse further from the surface before encountering an interstitial (and, conversely, interstitials are consumed by vacancies before they can reach the mask), leading to an offset of the substitutional peak from the surface by an angle $\theta_0 + \pi/2 = \pi\beta/\omega$.

## 5. Discussion

We first summarise some of the noteworthy features of the diffused profiles predicted by the results obtained here.

(1) Section 2.

In the surface-source problem there is a clear distinction between the case $D_v v^* > D_i i^*$ in which the impurity concentration becomes negligible in the narrow surface region $\widehat{x} = O(1)$ and the case $D_v v^* < D_i i^*$ in which the impurity penetrates much further and the substitutional profile contains a region of almost constant concentration (given by (27)). If we vary the surface concentration $i^*$, the expression (27), in principle, provides a means of obtaining information experimentally about parameters which are not susceptible to direct measurement. It is worth emphasizing that a qualitative change in the form of the impurity profile is predicted as $i^*$ is increased above $D_v v^*/D_i$. We note that, although the dissociative mechanism is mediated by vacancies, the impurity is thus able to diffuse much further when sufficiently few vacancies are available (*i.e.* when $v^* < D_i i^*/D_v$), since interstitials are then able to penetrate further before encountering a vacancy.

(2) Section 3.

In the implant case the moving boundaries can move in either direction and the qualitative appearance of the substitutional profile (which exhibits regions of rapid variation around the moving boundaries) depends strongly upon this. The results of Section 3.3.2 indicate the possibility of very high substitutional concentrations close to a slowly moving interface; those of Section 3.4 imply that the substitutional profile may exhibit high concentrations near the surface with a region of almost constant concentration further in. These are very distinctive types of profile and experimental results consistent with at least the latter are available.

(3) Section 4.

We have shown here that the ‘bird’s-beak’ profiles of [5] (which are similar to types which are observed experimentally) do not occur for all the relevant parameter regimes for the dissociative model. The substitutional profiles of Section 4.3 are again highly distinctive, exhibiting a region of significantly enhanced concentration in a particular direction $\theta = \theta_0$ close to the surface. Such predictions (as well as those indicated above) are potentially of value in clarifying which diffusion mechanisms are operating in practice. For example, ‘bird’s-beak’ structures appear to be much more robust for the kick-out mechanism (the other basic substitutional-interstitial mechanism, analysed by asymptotic methods in Meere and King [6]) than for the dissociative. The alternative type of behaviour outlined in Section 4 does not occur for kick-out and its observation would thus be indicative of the dominance of the dissociative mechanism.

We conclude by noting that this paper appears to represent the first instance where substitutional-interstitial models for solid-state diffusion have been formulated as moving-boundary problems. While the moving-boundary problems derived here are of a fairly simple type, it should be noted that the resulting formulations involve some important features (notably the determination of the leading-order substitutional profile) which do not occur in more familiar moving-boundary problems. Moving-boundary formulations are also applicable to much wider classes of diffusion mechanism, though the resulting problems may be significantly more complex (see [4]). The results of this paper open the way for the analysis of these more complicated models.

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## References

1. F.C. Frank and D. Turnbull, Mechanisms of diffusion of copper in germanium. *Phys. Rev.* 104 (1956) 617–618.
2. M.D. Sturge, A note on the theory of diffusion of copper in germanium. *Proc. Phys. Soc.* 73 (1959) 297–306.
3. M.G. Meere, J.R. King and T.G. Rogers, Asymptotic analysis of a model for substitutional-interstitial diffusion. *Z. angew. Math. Phys.* 45 (1994) 763–783.
4. M.G. Meere, Non-linear diffusion mechanisms in compound semiconductors. Ph.D. thesis, University of Nottingham, U.K. (1992).
5. M.G. Meere, J.R. King and T.G. Rogers, Asymptotic analysis of some two-dimensional diffusion problems. *Proc. Roy. Soc. Lond.* A448 (1994) 213–236.
6. M.G. Meere and J.R. King, An asymptotic analysis of a kick-out diffusion model. *Z. angew. Math. Phys.* 46 (1995) 546–565.