Rate Limitation at the Surface for Impurity Diffusion in Semiconductors

F. M. SMITS AND R. C. MILLER
Bell Telephone Laboratories, Murray Hill, New Jersey
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When a rate limitation exists at the surface for impurity diffusion in semiconductors, the appropriate boundary condition is equivalent to the radiation boundary condition for the conductance of heat in solids. The intentional introduction of an additional external rate limitation allows the measurement of partition coefficients. Solutions to the diffusion equation are summarized and the resulting impurity distributions are discussed.

INTRODUCTION

THE diffusion of impurities in single crystal semiconductor materials has been the subject of many investigations.[1-6] In most cases, the impurity was introduced at the surface from a suitable external phase. It was commonly assumed that the concentration of the diffusant in the semiconductor at the surface (hereinafter referred to as surface concentration) is in instantaneous equilibrium with the external phase, so that for an external phase constant in time, the distributions are described by erfc or erf[7] distributions or linear combinations of both. These distributions are solutions to Fick's Second Law, which is the differential equation describing a diffusion process for which the diffusion constant is independent of concentration.

For the special case of outward diffusion of impurities from a doped crystal into vacuum, an instantaneous equilibrium would lead to zero surface concentration at all times. To test if this condition applies, an n-type germanium crystal was grown doped with gallium and arsenic such that the concentration of arsenic was twice that of gallium. Samples of this crystal were heated in a high vacuum at a temperature of 850°C. With instantaneous equilibrium, the samples should develop a p skin immediately since the diffusion constant of gallium is two orders of magnitude smaller than the diffusion constant of arsenic.[1,3] However, only after several hours of heating could a p skin be observed. This can be interpreted as evidence that the rate of transport of arsenic across the solid-vacuum interface is limited by some process at the germanium surface which may be considered as a potential barrier which the impurity atoms must surmount to leave the crystal. A similar rate limitation was described by Barrer[8] for the ammonia-analcite system and by Drickamer and

co-workers[9,10] for liquid-liquid interfaces. The appropriate boundary condition is equivalent to the radiation boundary condition encountered in heat conduction problems. A theoretical analysis given here considers a rate limitation at the surface and also an additional rate limitation due to the external system. Experimental results will be reported in a subsequent paper.

BOUNDARY CONDITION WITH RATE LIMITATION

It is useful to define a partition coefficient

$$k_g = N_e/N_g, \tag{1}$$

where N_e is the concentration of impurity in the solid in equilibrium with the density N_g in the gaseous phase. The partition coefficient will be independent of concentrations if the gaseous phase can be treated as an ideal gas which is composed of atoms, and if the densities are low enough so that the semiconductor remains intrinsic.[11] Both conditions are generally fulfilled for the range of concentrations and temperatures over which diffusions of group III and group V elements are carried out.

An atom colliding with the surface has a certain probability s of entering the solid phase. The quantity s is commonly referred to as the sticking coefficient, and it can be expected that s is independent of concentration for the low densities of impurities usually encountered in semiconductors. The number of atoms entering the solid per cm² per sec equals $N_g s \bar{v}/4$, where $\bar{v}$ is the average thermal velocity of the atoms.

At equilibrium, the flow into the solid will be balanced by a flow out, and one can write:

$$N_e K = N_g s \bar{v}/4, \tag{2}$$

which defines a rate constant K. From (1) and (2), it follows that

$$K k_g = s \bar{v}/4. \tag{3}$$

Under the same conditions for which k_g and s are independent of concentration, K will be independent of concentration.

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[2] McAfee, Shockley, and Sparks, Phys. Rev. **86**, 137 (1952).
[3] W. C. Dunlap, Jr., Phys. Rev. **94**, 1531 (1954).
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[5] W. Boesenberg, Z. Naturforsch. **10a**, 285 (1955).
[6] C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. **27**, 544 (1956).
[7] $\mathrm{erf}x = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\xi^2)d\xi; \quad \mathrm{erfc}x = 1 - \mathrm{erf}x.$
[8] R. M. Barrer, *Diffusion in and Through Solids* (Cambridge University Press, Cambridge, 1951).
[9] L. H. Tung and H. G. Drickamer, J. Chem. Phys. **20**, 6 (1952).
[10] J. H. Sinfelt and H. G. Drickamer, J. Chem. Phys. **23**, 1095 (1955).
[11] Reiss, Fuller, and Morin, Bell System Tech. J. **35**, 535 (1956).

Generally, the concentration in the solid will be a function of the depth x and the time t and will be written as $N(x,t)$. If the surface concentration $N(0,t)$ differs from the equilibrium concentration N_e the flow out of the crystal will be $N(0,t)K$; thus, a net flow across the surface results. This net flow must produce a diffusion flow $[-D\partial N(x,t)/\partial x]_{x=0}$ within the solid, where D is the diffusion constant. Thus, one obtains the boundary condition,

$$[N_e-N(0,t)]K=[-D\partial N(x,t)/\partial x]_{x=0}, \quad (4)$$

which is equivalent to the radiation boundary condition encountered in the theory of heat conduction.[12] This boundary condition was applied to the systems mentioned previously.

The rate constant K describes the rate limitation at the surface of the solid. The material entering or leaving the surface tends to change the density N_g in the gaseous phase so that the condition of a constant external phase is only fulfilled if the density N_g is maintained by some external flow. An additional external rate limitation would make N_g time-dependent. It will be shown that the intentional introduction of such an external rate limitation enables the determination of k_g.

As an idealized arrangement, consider a sample in a container of volume V which is connected to a vacuum pump through a flow resistance with a resulting pumping speed L (Fig. 1), and let a constant flow F_1 of vapor enter the box. If there is no sink for the vapor inside the box, a flow F_2, equal to F_1, leaves the box in the steady state. The density in the box under these conditions is

$$N_g=F_1/L. \quad (5)$$

A crystal whose impurity concentration is $N_e=N_gk_g$ would be in equilibrium with the vapor in the box.

$$N_e=N_gk_g=F_1k_g/L. \quad (6)$$

If, however, the crystal has a surface concentration smaller than N_e, a flow F_3 into it results. The density in the box will then be changed to some other value $N_g'\neq N_g$ since now $F_2\neq F_1$. Due to the diffusion processes, F_3 and thus N_g' will be time dependent. If the time constant V/L is short, compared to the rate of change of F_3, one can neglect a term equal to $V\partial N_g'/\partial t$ and one obtains

$$F_1=F_2+F_3. \quad (7)$$

The boundary condition for this case becomes:

$$[N_g'k_g-N(0,t)]K=[-D\partial N(x,t)/\partial x]_{x=0}. \quad (8)$$

The time-dependent quantity N_g' can be eliminated by using Eq. (6), Eq. (7), $F_2=N_gL$, and $F_3/A=[-D\partial N/\partial x]_{x=0}$, where A designates the surface area of the
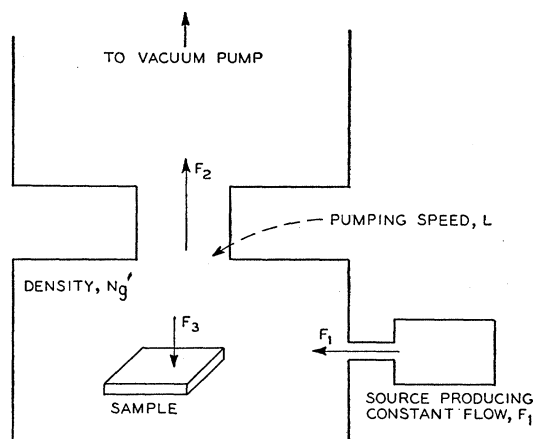
[12] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1948).

FIG. 1. External rate limitation.

crystal. The boundary condition then becomes:

$$[N_e-N(0,t)]\left(\frac{L}{L+k_gKA}\right)K=\left[-D\frac{\partial N(x,t)}{\partial x}\right]_{x=0}. \quad (9)$$

This condition is equivalent to (4) with a modified rate constant

$$K'=\left(\frac{L}{L+k_gKA}\right)K. \quad (10)$$

From an experimental determination of K' for different L and A, one can obtain K and k_g. The sticking coefficient s follows from Eq. (4).

SOLUTIONS TO THE DIFFUSION EQUATION

To obtain the distribution of a diffusant in the solid, the diffusion equation has to be solved subject to the boundary condition given in Eq. (4). The solutions for similar heat flow problems[12] are applicable with a proper change in variables. For the diffusion of impurities in semiconductors the most important geometry is the semi-infinite solid. The solutions are more easily expressed in terms of the following parameters:

$$y=x/2(Dt)^{\frac{1}{2}}, \quad z=(Dt)^{\frac{1}{2}}K/D. \quad (11)$$

The more important solutions are

Case 1.—Constant density in the gaseous phase, $N_g=N_e/k_g$. Zero initial concentration in the solid, $N_0=0$.

$$N(y,z)/N_e=\exp(-y^2)\{\exp(y^2)\,\text{erfc}y$$
$$-\exp[(y+z)^2]\,\text{erfc}(y+z)\}=f_1(y,z). \quad (12)$$

Case 2.—Zero concentration in the gaseous phase $N_g=N_e=0$. Uniform initial concentration N_0 in the solid.

$$N(y,z)/N_0=1-f_1(y,z)=f_2(y,z). \quad (13)$$

Case 3.—Zero concentration in the gaseous phase $N_g=N_e=0$. Sheet source of sheet density $\bar{N}_0$ initially

in the surface of the solid.

$$N(y,z)(\pi Dt)^{\frac{1}{2}}/\bar{N}_0 = \exp(-y^2)\{1 - \pi^{\frac{1}{2}}z \exp[(y+z)^2]$$
$$\times \mathrm{erfc}(y+z)\} = f_3(y,z). \quad (14)$$

A graph of the solution to Case 1 can be found in reference 12, p. 54.[13] Two asymptotic forms of the solution are:

$$\lim_{z\to\infty} f_1(y,z) = \mathrm{erfc}\, y, \text{ which corresponds to a}$$

constant surface concentration N_e, (15)

$$\lim_{z\to 0} f_1(y,z) = 2z \int_y^\infty \mathrm{erfc}\,\xi\, d\xi, \text{ which corresponds to a}$$

constant flux $N_e K$ across the surface. (16)

The second asymptotic solution is a slightly steeper distribution than the erfc-distribution. The surface concentration of such a distribution is $N(0,z) = N_e 2z/\sqrt{\pi}$. The asymptotic forms of the solution to Case 3 are the Gaussian distribution $\exp(-y^2)$ and zero corresponding to z very small and very large, respectively.

An important quantity for a diffused surface layer is the total amount, $\bar{N}$, per cm² diffused into the solid. This requires the integration of the distribution. The integrals have the form[13]:

Case 1:

$$\bar{N}(t) = \int_0^\infty N(x,t)dx$$

$$= N_e 2(Dt)^{\frac{1}{2}}\left(\frac{1}{\sqrt{\pi}} - \frac{1}{2z}[1 - \exp(z^2)\,\mathrm{erfc}\,z]\right)$$

$$= N_e 2(Dt)^{\frac{1}{2}}F_1(z). \quad (17)$$

Case 3:

$$\bar{N}(t) = \int_0^\infty N(x,t)dx = \bar{N}_0 \exp(z^2)\,\mathrm{erfc}\,z = N_0 F_3(z). \quad (18)$$

Case 2 describes a diffusion-out process. The total amount diffused out as a function of time is given by the integral for Case 1, in which N_e is replaced by N_0.

EVALUATION OF DIFFUSED LAYERS

If a conductivity-determining impurity is diffused into a semiconductor of opposite conductivity type, a p-n junction occurs where the concentration of the diffused material equals the concentration of the body-doping N_b. Owing to diffusion out, N_b tends to decrease towards the surface. If, however, the ratio between N_b and the surface concentration $N(0)$ of the diffusant is sufficiently small, N_b is unchanged at the junction.

If the impurity distribution in the layer is known,

one can deduce the surface concentration $N(0)$ from the layer thickness and the total sheet density $\bar{N}$ in the diffused distribution, which is related to the sheet resistivity of the layer. For diffusion with rate limitation at the surface, the shape of the distribution varies between the two asymptotic functions (15) and (16). For these distributions, Fig. 2 gives $N(0)/N_b$ as a function of $\bar{N}/aN_b$ where a is the thickness of the conversion layer.

DISCUSSION

With a rate limitation at the surface, a finite flow $N(0)K$ leaves the surface. This flow should be compared with the flow of atoms arriving at the surface from inside the solid. In the one-dimensional kinetic theory of diffusion,[14] the total number of atoms migrating in a given direction is expressed in the general form $N(x)\lambda p$, where λ is the average jump distance and p the probability that an atom jumps in the given direction per unit time. In these terms the diffusion constant takes the form $D = \lambda^2 p$, which allows one to express p without considering the detailed theory of the particular diffusion mechanism. The flow of atoms migrating in a given direction, therefore, can be written as $N(x)D/\lambda$; and one obtains for the ratio:

$$\frac{\text{flow leaving the solid}}{\text{diffusion flow towards the surface}} = \left(\frac{K}{D}\right)\lambda. \quad (19)$$

This expression can be interpreted as the ratio between a probability p_0 that an atom leaves the solid from a surface site and the probability p for a jump inside
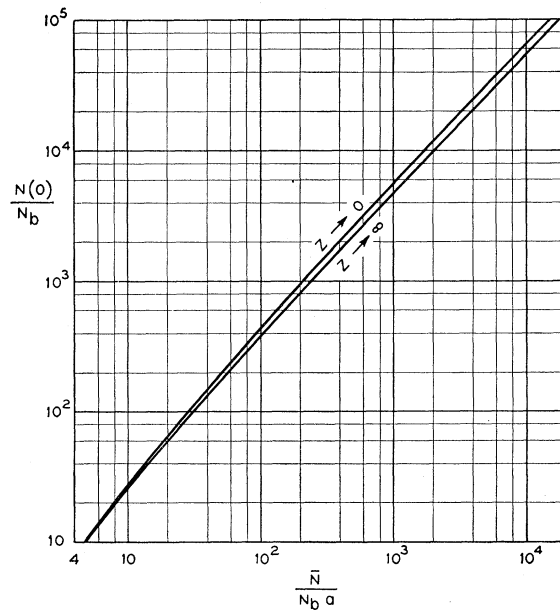
FIG. 2. Evaluation of surface concentrations.

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[13] The functions $f_1(y,z)$, $f_3(y,z)$, $F_1(z)$, and $F_3(z)$ were tabulated. Copies are available on request.

[14] See, for example, R. M. Barrer, Trans. Faraday Soc. **37**, 590 (1941).

the lattice. The rate constant K takes the form

$$K = p_0 \lambda. \qquad (20)$$

It is reasonable to assume that an impurity jumps only from one site to a nearest neighbor site for the diffusion of group III and group V elements in group IV semiconductors. The average jump distance is then slightly different in the various crystal directions. For germanium, $\lambda = 1.5 \times 10^{-8}$ cm is an average figure.

From the experiments mentioned in the beginning, it follows that p_0/p is of the order 10^{-5} for arsenic in germanium. More specific experimental results will be reported in a subsequent paper.

Solid State Luminescence Theory and Oscillator Strengths in KCl:Tl[†]

R. S. KNOX[*] AND D. L. DEXTER
Institute of Optics, University of Rochester, Rochester, New York
(Received August 27, 1956)

The existing quantitative treatment by Williams of the Seitz model for the KCl:Tl luminescent system has been extended to include a prediction of the oscillator strengths of the 1960 A and 2475 A absorption lines. These f values are simply related to those of the associated free-ion transitions. In the course of the computations it is found that the best available Tl$^+$ wave functions are inaccurate for the free ion and are therefore not of great value for the KCl:Tl center. Free-ion oscillator strengths are (a) computed with these functions and are (b) estimated by analysis of experimental spectra; the results of both methods, when modified for KCl:Tl, are in poor agreement with experimental f values in the solid. A review and critique are given for the present Williams dynamical treatment of the Seitz-Williams model, and

it is concluded that a sensitive test for the model would be its successful prediction of the ratio of these (1960 A and 2475 A) oscillator strengths in KCl:Tl; the observed values are from three to five times as large as the predicted value. We conclude that the KCl:Tl problem is not as well understood as it has been believed, since the existing quantitative theory (a) is subject to considerable arbitrariness in the construction of excited-state configurational coordinate curves, (b) appears to be in fortuitous agreement with experiment insofar as its quantitative predictions depend on thallous ion wave functions, and (c) does not, in our simple extension, predict the observed ratio of oscillator strength corresponding to the electronic transitions assumed responsible for the behavior of the center.

I. INTRODUCTION

THE task of an absolute theory of solid state luminescence is by no means a small one. We should expect to obtain from it a quantitative description of a luminescent system sufficiently complete that absorption and emission could be attributed to specific electronic processes, and that transition probabilities, quantum yields, line shapes, and energy levels could be accurately computed from the wave functions of the system. The semiclassical Franck-Condon principle may be called upon to reduce the initial complexity of such a problem, and Lax[1] has considered its application to crystalline systems. Under this principle, which is applicable to many systems in which the Born-Oppenheimer approximation holds, the detailed computation of an absorption or emission spectrum separates into three parts: (1) the total energy change $E_b(x) - E_a(x)$ of the system when an electronic transition $a \to b$ occurs at a nuclear configuration described by a set of coordinates x, (2) the matrix elements $H_{ba}'(x)$ of all radiative and nonradiative perturbing Hamiltonians, and (3) the statistical distribution, $P_a(x)$, of the initial nuclear

states $X_a(x)$. In spite of the large number of possibly relevant coordinates in x, it has been found that a small number of them, sometimes only one, can be used to explain the behavior of some of the simpler inorganic phosphors.[2-4]

In the one serious attempt to treat this problem, or at least part of it, for a specific case, Williams[3] has considered the system KCl:Tl, on the basis of the electronic energy level scheme proposed by Seitz.[2] He has obtained functions E_b and E_a corresponding to the $^3P_1$ and $^1S_0$ free thallous ion states, which, when combined with the distribution function appropriate to the associated vibrational mode, predict fairly well the positions[3] and temperature dependence of the widths[5] of the 2475 A absorption and 3050 A emission lines of KCl:Tl. Thus parts (1) and (3) of the problem (see above) have been considered. (A configuration coordinate curve linking the 1960 A absorption and 4780 A emission of this center with the $^1P_1 - ^1S_0$ free Tl$^+$ transition has also been developed[6] by fitting the experimental spectra. See, however, Sec. IV.)

It seemed important to extend Williams' theoretical

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