Rothman for their interest and encouragement during its completion. O. Almén and R. Kelly provided their recent unpublished data, and pointed out some of the numerous errors in a preliminary version of this manuscript. With D. Onderdelinde, I had an inspiring correspondence on a controversial subject. My special thanks are due to H. H. Andersen, J. A. Davies, C. Lehmann, J. B. Sanders, and K. B. Winterbon, with whom I had the opportunity to cooperate on many problems that are related to this work, and to Mrs. Vera Heitsch, who patiently and efficiently typed several editions of the paper.

PHYSICAL REVIEW VOLUME 184, NUMBER 2 10 AUGUST 1969

Deep Multistream Diffusion in Ion Implantation*

M. Sparks

Science Center, North American Rockwell Corporation, Thousand Oaks, California 91360

(Received 6 February 1969)

Very deep penetration of ions injected into crystals has been reported in several recent experiments. These "supertails," which extend deeper into the crystals than the normal stopping range or channeling range, have the form $n_s \sim (x-x_0)^{-\eta}$, where n_s is the number of incident ions per cm^3, x is the distance from the surface of the crystal, η is typically $\sim$2–8, and x_0 is $\sim 1\ \mu$ or less. Multistream steady-state-diffusion models are developed to explain these supertails. The results agree well with published experimental data. Multistream diffusion may also be involved in other experiments, such as radiation-enhanced diffusion experiments and implantation experiments in which channeling is suppressed, but the measured concentration profiles are within the maximum channeling range.

1. INTRODUCTION

When heavy ions with energies less than 1 MeV are injected into a crystal, they are stopped near the surface of the crystal, typically within a fraction of a micron.[1] But in some special cases, measurements[2–8] of the number n_S of implanted ions per cm^3 have revealed large concentrations much deeper (up to 10 μ) than the normal stopping region. All of these supertails observed to date have the form $n_S \sim (x-x_0)^{-\eta}$, with $\eta = 2$–8, where x is the distance into the crystal measured from the surface.

Although channeling[9] affords one explanation of penetration up to depths of $\sim 1\ \mu$, the supertails extending several microns deep are almost certainly not caused by channeling.[4] Previous explanations of these supertails have involved either a single-stream diffusion with a constant number of traps[4,10] or superdeep channeling.[11,12] The exponential concentration predicted by the single-stream constant-trap model could conceivably be modified by a variation in the concentration of trapping centers with distance from the sample surface, but a change of the shape of n_S from exponential to power law for four orders of magnitude change in n_S and for different samples is highly unlikely. The possibility of anomalously deep penetration due to the periodicity of the lattice has also been discussed by De Wames, Hall, and Lehman,[13] and the effect of the crystal binding of target atoms on the scattering process has been considered by De Wames and Hall.[14]

A theory is presented which explains all supertail experiments known to the author. The power-law profiles are explained by a general diffusion model, suggested by McCaldin,[15] in which several species such as vacancies, self-interstitials, and implanted ions all diffuse so rapidly that a steady state is maintained throughout the bombarding time. Kornelsen *et al.*[3] also suggested that interstitial diffusion which is stopped by vacancies might be important.

---

* Research performed in part at the Hughes Research Laboratories, Malibu, Calif.

[1] J. Lindhard and M. Scharff, Phys. Rev. **124**, 128 (1961). This theory, developed for gases and amorphous solids, has been supplied successfully to crystals in the normal stopping region (excluding channeling and diffusion).

[2] B. Domeij, F. Brown, J. A. Davies, G. R. Piercy, and E. V. Kornelsen, Phys. Rev. Letters **12**, 363 (1964).

[3] E. V. Kornelsen, F. Brown, J. A. Davies, B. Domeij, and G. R. Piercy, Phys. Rev. **136**, A849 (1964).

[4] J. A. Davies and P. Jespersgard, Can. J. Phys. **44**, 1631 (1966).

[5] J. A. Davies, L. Eriksson, and J. L. Whitton, Can. J. Phys. **46**, 573 (1968).

[6] H. Herrmann, H. Lutz, and R. Sizmann, Z. Naturforsch. **21A**, 365 (1966).

[7] R. W. Bower, R. Baron, J. W. Mayer, and O. J. Marsh, Appl. Phys. Letters **9**, 203 (1966).

[8] O. Meyer, Nucl. Instr. Methods **70**, 285 (1969).

[9] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **34**, No. 14 (1965). See Refs. 2 and 4 for convincing channeling experiments and for references to previous channeling literature.

[10] J. O. McCaldin, *Progress in Solid State Chemistry* (Pergamon Press Ltd., London, 1965), Vol. 2, p. 9.

[11] C. Erginsoy, Phys. Rev. Letters **12**, 366 (1964).

[12] J. O. McCaldin and J. A. Brinkman, Phys. Letters **17**, 221 (1965).

[13] R. E. De Wames, W. F. Hall, and G. W. Lehman, Phys. Rev. **148**, 181 (1966).

[14] R. E. De Wames and W. F. Hall, Phys. Rev. Letters **17**, 125 (1966).

[15] J. O. McCaldin (private communication).

In addition to explaining the recent experimental results, the present theory affords a new method of measuring diffusion constants and binding energies of damage centers which are otherwise difficult to measure, and it offers a method of tailoring different types of concentration profiles such as e^{-x^2}, e^{-kx}, or $(x+x_0)^{-\eta}$. The theory may also be related to the radiation-enhanced diffusion experiments of Pfister and Baruch,[16] Strack,[17] and Glotin,[18] and to implantation experiments,[19–22] where channeling is suppressed, but where the measured concentration profiles are within the maximum channeling range.

Although the agreement between the theory and experiments is convincing evidence for the validity of the theory, and although there now seems to be little doubt that diffusion is involved in the supertails, experiments designed specifically to test the details of the various models would be useful. A preliminary report of these results has been given elsewhere.[23]

2. PHYSICAL MODELS

In the general multistream-diffusion model, several species, such as implanted ions, vacancies, self-interstitials, impurity ions, etc., diffuse and may combine with one another while diffusing. The resulting nonlinear diffusion equations can be solved in some simple cases. In all cases which are solved here, the concentrations of the primary diffusing species approach constants as the time $t\rightarrow\infty$, and it is this steady-state solution which is found.

As the first example of the general multistream-diffusion model, consider the "V-I-B model." When ions of energy E strike a crystal, some are stopped in interstitial sites and others in substitutional sites. It is assumed that (A) every bombarding ion produces many vacancies V and *self*-interstitials I. The region near the surface of the crystal where the bombarding ions are stopped and the vacancies and interstitials are created, called the generation region, extends into the sample a distance l, which is typically a fraction of a micron.[1] The self-interstitials I, vacancies V, and bombardant interstitials B then diffuse out of the generation region. An interstitial bombardant ion may encounter a vacancy and form a substitutional bombardant ion S. A self-interstitial may also encounter a vacancy and form a substitutional host ion; i.e., the vacancy and self-interstitial are annihilated. Symbolically, $B+I=S$ and $V+I=0$.

It is assumed (B) that the bombardant *substitutional* ions either diffuse so slowly that they may be considered as fixed in place or are trapped by an impurity, dislocation, etc., before they diffuse very far. The self-interstitials, vacancies, and bombardant *interstitial* ions are assumed to diffuse so rapidly that (C) their concentrations are maintained at their steady-state values during most of the bombarding time, which is typically a few minutes. An order-of-magnitude argument (Appendix C) indicates that in a typical experiment the diffusion constants of the vacancies, self-interstitials, and interstitials must be larger than $\sim 10^{-10}$ cm^2 sec^{-1} in order for the steady state to be established in a small fraction of the implantation time.

If the numbers of vacancies and self-interstitials are much larger than the number of bombardant interstitials [assumption (A)], the two-stream diffusion equations of the V's and I's, which are relatively unaffected by the small number of B's, can be solved for the concentration n_V of V's. The B's diffuse and are trapped by this fixed concentration n_V. In Sec. 3, it will be shown that the steady-state vacancy concentration n_V either (i) decreases as the inverse square, (ii) is constant, or (iii) decreases exponentially as the distance x from the surface of the crystal increases, depending on the experiment. In case (i), the number n_B of interstitial bombardants per cm^3 will be given by $n_B\sim(x-l+d)^{-r}$ for $x>l$, and in cases (ii) and (iii), n_B will decrease exponentially.

The number n_S of substitutional bombardant ions per cm^3 is determined by combining the bombardant interstitials with the vacancies; thus,

$$\partial n_S/\partial t=\beta_{VB}n_Vn_B\,,$$

where β_{VB}, which we call a combination coefficient, is assumed to be independent of n_V and n_B. Integrating this equation from $t=0$ to $t=\tau$ (the implantation time) gives

$$n_S=\tau\beta_{VB}n_Vn_B\sim(x-l+d)^{-(2+r)} \tag{1}$$

for case (i), and gives exponential n_S for cases (ii) and (iii). A single-stream model,[4,10] in which diffusing B's are trapped by a constant concentration of trapping centers, also gives an exponential profile.

Next, consider the "I-I-B model." If the vacancies are not mobile at the implantation temperature T, but the self-interstitials are mobile and can combine with one another to form di-interstitials which do not affect the I diffusion, then the self-interstitial diffusion establishes an inverse-square concentration of self-interstitials. There are several reasons why the di-interstitial may not affect the diffusion of the I's and B's. Since the di-I's build up linearly in time (while the I's are in the steady state), for a short implantation time τ the concentration of di-I's will be negligible.

---

[16] J. C. Pfister and P. Baruch, J. Phys. Soc. Japan **18**, Suppl. III, 251 (1963).

[17] H. Strack, J. Appl. Phys. **34**, 2405 (1963).

[18] P. M. Glotin, Can. J. Phys. **46**, 705 (1968).

[19] J. A. Davies, G. C. Ball, F. Brown, and B. Domeij, Can. J. Phys. **42**, 1070 (1964).

[20] J. F. Gibbons, A. El-Hoshy, K. E. Manchester, and F. L. Vogel, Phys. Letters **8**, 46 (1966).

[21] G. Dearnaley, J. H. Freeman, G. A. Gard, and M. A. Wilkins, Can. J. Phys. **46**, 587 (1968).

[22] W. Kleinfelder, W. S. Johnson, and J. Gibbons, Can. J. Phys. **46**, 597 (1968).

[23] M. Sparks, Phys. Rev. Letters **17**, 1247 (1966).

Diffusion of the di-I's will further prevent a buildup in their concentration. Trapping of the di-I's by point defects, dislocations, etc., will also retard their buildup. The B's, which could be either interstitial or substitutional bombardants in this case, are then trapped by the I's with their inverse-power-law concentration dependence.

The analogous situation with nondiffusing I's and diffusing V's could also occur, giving the "V-V-B model." If only the B's diffuse and they combine with one another to form di-B's, the resulting model is called the "B-B model." A two-stream diffusion of V's (or I's) and B's with the V's (or I's) combining with the B's to give an immobile or quickly trapped complex is another possibility. This is labeled the "V-B model" (or the "I-B model").

Still other models within this multistream-diffusion framework are possible. For instance, the B's could diffuse substitutionally and combine with I's rather than V's, in the V-I-B model; or, in general, the B's could diffuse as either interstitial or substitutional bombardants which combine with V's and/or I's. Furthermore, the pair resulting from this combination, such as the B-I pair, could be mobile or immobile. If it is either immobile or mobile but trapped in a short distance by a dislocation, impurity, etc., the analysis below is valid. But if the pair is mobile and diffuses a long distance, the analysis and resulting concentration profile will be complicated in general. It is conceivable that other types of damage centers are involved in the multistream-diffusion process, especially if the surface or generation region contains a high concentration of impurities.

As an example of other considerations which may be involved in the general multistream-diffusion model, suppose that $D_V \gg D_I$ in the V-I-B model. We shall see that the number of self-interstitials can be much larger than the number of vacancies in this case because the vacancies diffuse away rapidly. Thus, if the self-interstitials combine with each other as readily as they combine with the vacancies, and if the B's and I's combine with each other as readily as the B's and V's do, it would be appropriate to consider the I-I-B model in this case. Similarly, if $D_I \gg D_V$ and the V-V and V-I formation processes were comparable, it would be inappropriate to consider the V-V-B model.

3. SOLUTION OF DIFFUSION EQUATIONS

In this section the diffusion equations are solved for the number n_S of bombardant ions per cm^3 in the supertail. First consider the three-stream V-I-B model. The diffusion equations describing the model are [with the time derivatives equal to zero according to assumption (C)]

$$\frac{\partial n_V}{\partial t}=0=D_V\frac{d^2n_V}{dx^2}-\beta_{VI}n_Vn_I+G(x)-\beta_{VB}n_Vn_B\,, \qquad (2)$$

$$\frac{\partial n_I}{\partial t}=0=D_I\frac{d^2n_I}{dx^2}-\beta_{VI}n_Vn_I+G(x)\,, \qquad (3)$$

$$\frac{\partial n_B}{\partial t}=0=D_B\frac{d^2n_B}{dx^2}-\beta_{VB}n_Vn_B+G_B(x)\,, \qquad (4)$$

where the D's are diffusion constants, the β's are combination coefficients, and the subscripts V, I, and B denote vacancy, self-interstitial, and bombardant interstitial, respectively.

The thermal equilibrium (zero flux of bombarding particles) concentrations are neglected since they are small and unrelated to the present diffusion process. The functional form of $G(x)$, which is the rate of the creation of vacancies and of self-interstitials, depends on many factors, such as the energy and type of bombarding ion and the type of target ion. Since the generation region is defined by $0<x<l$, it follows that $G(x)=0$ for $x>l$. The same generation function $G(x)$ appears in (2) and (3), since the vacancies and self-interstitials are created in pairs.[24]

When many vacancy–self-interstitial pairs are created by every bombarding ion, or more precisely, when the condition $\beta_{VB}n_B \ll \beta_{VI}n_I$ is satisfied, the term $\beta_{VB}n_Vn_B$ in (2) can be neglected and (2) and (3) can be solved independently of (4). In this case, subtracting (3) from (2) and integrating twice gives

$$D_Vn_V(x)-D_In_I(x)=D_Vn_V(l)-D_In_I(l)+[J_I(l)-J_V(l)](x-l)\,, \qquad (5)$$

where the diffusion currents J are equal to $-Ddn/dx$. If the I and V currents crossing the plane $x=l$ are equal, the last term in (5) vanishes, giving

$$D_Vn_V(x)-D_In_I(x)=RD_Vn_V(l)\,, \qquad (6)$$

where

$$R\equiv[D_Vn_V(l)-D_In_I(l)]/D_Vn_V(l)\,. \qquad (7)$$

This assumption of equal currents is satisfied exactly if the I's and V's are created and annihilated in pairs. In reality there are several factors which could give $\Delta J\equiv J_I(l)-J_V(l)\neq 0$. A high concentration of impurity ions in the generation region would reduce the rate of generation of self-interstitials, since some of the generated interstitials would be impurities. If the annihilation of the V's and I's were not controlled by the process $V+I=0$, the annihilation rates of V's and I's could be different. For example, unequal annihilation

---

[24] A particular ion which is knocked out of a substitutional site, leaving a vacancy, will in general stop in an interstitial site at some distance from the vacancy. Consequently, the two generation functions are not exactly equal, although this should be a small effect.

of V's and I's at the surface of the sample could cause unequal currents at $x=l$. Since this would require diffusion of V's or I's to surface, unequal absorption at the surface, and diffusion from the surface to $x=l$, this source of ΔJ is expected to be small. The creation of I-I or V-V defects would give $\Delta J\neq 0$. If the I-I or V-V formation completely dominated the $I+V=0$ process, the I-I-B or V-V-B model would be appropriate. The solutions for the intermediate cases, in which one of the processes does not dominate the other two, have not been found. Finally, it should be mentioned that the assumption of $\Delta J=0$ is necessary only in the V-I-B model.

Eliminating n_V from (3) by using (6) gives

$$0=D_I\frac{d^2n_I}{dx^2}-\beta_{VI}\frac{D_I}{D_V}n_I^2-\beta_{VI}Rn_V(l)n_I+G(x). \tag{8}$$

This nonlinear differential equation can be solved in the region $l<x$ where $G=0$ by using an energy integral.[25] That is, multiplying by dn_I/dx and integrating reduces (8) to a first-order equation, which is easily solved to give

$$n_I(x)=n_I(l)\left(\frac{1-e^{-kL}}{1-e^{-k(x-l+L)}}\right)^2e^{-k(x-l)}, \tag{9}$$

where

$$k\equiv[\beta_{VI}Rn_V(l)/D_I]^{1/2} \tag{10}$$

and

$$L\equiv\frac{1}{k}\ln\frac{[n_I(l)+N]^{1/2}+N^{1/2}}{[n_I(l)+N]^{1/2}-N^{1/2}},\quad N\equiv\frac{3D_Vn_V(l)R}{2D_I}. \tag{11}$$

The expression for n_V is determined by (6) and (9). We have assumed that R is positive. For negative R, Eqs. (7) and (9)–(11) are valid if the V and I subscripts are interchanged.

For $R=0$, which is shown in Appendix A to be the most common case, results (9) and (6) give[26]

$$n_V(x)=\frac{D_I}{D_V}n_I(x)=n_V(l)\left(\frac{d_0}{x-l+d_0}\right)^2, \tag{12}$$

where

$$d_0\equiv\lim_{R\to 0}L=\left(\frac{6D_I}{\beta_{VI}n_V(l)}\right)^{1/2}=\left(\frac{6D_V}{\beta_{VI}n_I(l)}\right)^{1/2}. \tag{13}$$

The number n_B of interstitial bombardants is determined by (4). For n_V given by (12), the solution of (4) for $x>l$ is

$$n_B(x)=n_B(l)\left(\frac{d_0}{x-l+d_0}\right)^{r_0}, \tag{14}$$

where

$$r_0(r_0+1)=6\beta_{VB}D_I/\beta_{VI}D_B. \tag{15}$$

The number n_S of substitutional implanted ions is determined by (1), (12), and (14):

$$n_S(x)=\beta_{VB}\tau n_V(l)n_B(l)\left(\frac{d_0}{x-l+d_0}\right)^{2+r_0}\quad\text{for } R=0. \tag{16}$$

The corresponding results for the case of $R\cong 1$ are

$$n_I(x)\cong n_I(l)e^{-k(x-l)},$$

$$n_V(x)=Rn_V(l)+(D_I/D_V)n_I(x)\cong n_V(l), \tag{17}$$

$$n_B(x)\cong n_B(l)e^{-k_B(x-l)}, \tag{18}$$

and

$$n_S(x)=\beta_{VB}\tau n_V(l)n_B(l)e^{-k_B(x-l)}, \tag{19}$$

where

$$k_B=\left(\frac{\beta_{VB}n_V(\infty)}{D_B}\right)^{1/2}\cong\left(\frac{\beta_{VB}n_V(l)}{D_B}\right)^{1/2}.$$

In the last equality in (17), we have used

$$\frac{D_In_I(x)}{RD_Vn_V(l)}\leq\frac{D_In_I(l)}{RD_Vn_V(l)}=\frac{1-R}{R}\ll 1. \tag{20}$$

For $R=0$, n_S has the power-law profile, while for $R\cong 1$, n_S has the exponential profile.

These results can be simplified by writing the bombardant interstitial current $J_B(l)$ at the plane $x=l$ as $J_B(l)=fJ_0$, where J_0 is the current of bombardant ions incident on the crystal and where f is the fraction of these ions which cross the plane $x=l$. Using this result as well as $J_B(l)=-D_B(dn_B/dx)_{x=l}$ and (14), we find that $n_B(l)=fd_0J_0/r_0D_B$. Using this result, (13), and the similar results for the case of $R\cong 1$, reduces (16) and (19) to the central results

$$n_S(x)=fJ_0\tau\frac{r_0+1}{d_0}\left(\frac{d_0}{x-l+d_0}\right)^{2+r_0}\quad\text{for}\quad R=0 \tag{21}$$

$$=fJ_0\tau k_Be^{-k_B(x-l)}\quad\text{for}\quad R\cong 1. \tag{22}$$

Integrating from $x=l$ to ∞ gives $N_{\text{tot}}=fJ_0\tau$ for the total number of ions in the tail, which is correct, since particles are conserved. By using (13), the derivative of (12), and $J_V(l)=-D_V(dn_V/dx)_{x=l}$, we obtain

$$d_0=\left(\frac{12D_VD_I}{\beta_{VI}J_V(l)}\right)^{1/3}. \tag{23}$$

We now argue that d_0 will not be very strongly dependent on E and J_0. If the number of vacancies created by a bombarding ion were proportional to the energy E of the ion, and if the fraction of the created vacancies which reach the $x=l$ plane before combining with a self-interstitial were independent of J_0, E, and T (and therefore independent of the number of self-interstitials in the generation region), then $J_V(l)$ would be proportion EJ_0. Since neither of these assumptions

---

[25] G. A. Korn and T. M. Korn, *Mathematical Handbook For Scientists and Engineers* (McGraw-Hill Book Co., New York, 1961), p. 270.

[26] This central result (12) can be obtained directly by substituting (6) with $R=0$ into (2) and writing down the well-known answer from classical mechanics.

is true, d_0 will vary less strongly with E and J_0 than $(1/EJ_0)^{1/3}$, according to (23). In other words, d_0 will decrease only slightly when E or J_0 is increased; doubling the energy should cause a decrease in d_0 of less than 25%.

The results above for the specific *V-I-B* model are easily generalized to other cases. For example, for the *I-I-B* model, (3) is replaced by [see Appendix B, Eq. (41)]

$$D_I d^2 n_I/dx^2 - \beta_{II} n_I^2 = 0, \tag{24}$$

where β_{II} is the combination coefficient for the I's with themselves, and where $G=0$ outside the generation region. The solution to (24) is

$$n_I = n_I(l)\left(\frac{d_I}{x-l+d_I}\right)^2, \quad d_I \equiv \left(\frac{6D_I}{\beta_{II} n_I(l)}\right)^{1/2}. \tag{25}$$

For the combination of the B's and I's, Eq. (4) is valid if n_V is replaced by n_I and β_{VB} by β_{IB}; thus

$$n_B = n_B(l)\left(\frac{d_I}{x-l+d_I}\right)^{r_I}, \tag{26}$$

where

$$r_I(r_I+1) = 6\beta_{IB} D_I/\beta_{II} D_B. \tag{27}$$

Equation (1) becomes $n_S = \tau\beta_{IB} n_I n_B$ for the *I-I-B* model, where n_S is the number of *I-B* pairs per cm^3, i.e., the number of bombardant ions per cm^3 in the supertail. This equation with (25) and (26) gives

$$n_S(x) = \tau\beta_{IB} n_I(l) n_B(l)\left(\frac{d_I}{x-l+d_I}\right)^{2+r_I}. \tag{28}$$

Repeating the analyses which gave (21) and (23) for the present case gives

$$n_S(x) = fJ_0\tau\frac{r_I+1}{d_I}\left(\frac{d_I}{x-l+d_I}\right)^{2+r_I} \tag{29}$$

and

$$d_I = \left(\frac{12D_I^2}{\beta_{II} J_I(l)}\right)^{1/3}. \tag{30}$$

In the *I-I-B* model, diffusion of the *I-B* pairs would change the concentration (28). It is reasonable to assume that an *I-B* pair is less mobile than a single B. Furthermore, the *I-B* pairs may combine with I's, and the *I-I-B* damage center should be still less mobile, etc. Consequently, it seems quite reasonable that the distance that a B (in an *I-B* or *I-I-B*, etc., damage center) diffuses from the position where the *I-B* pair is formed is sufficiently short; that is, the concentration (28) is not changed by the subsequent diffusion of the *I-B* pairs. For example, if we consider the diffusion of *I-B* pairs from a given position x_1 with a given current $-D_p(dn_p/dx)_{x=x_1}$, the resulting concentration is $n_p \sim (x-x_1+d)^{r_p}$, where $r_p(r_p+1) = 6\beta_{pI} D_I/\beta_{II} D_p$. If β_{pI} is of the order of or greater than β_{II}, and if $D_p \ll D_I$ as expected, then $r_p \gg 2$; i.e., the *I-B* pairs do not diffuse far.

The results for the *V-V-B* model are obtained from (29), (30), (25), and (27) simply by replacing I by V.

4. SUMMARY OF THEORETICAL RESULTS

(*a*) *Form of the supertails.* The central result is that the number n_S of bombardant ions per cm^3 in the supertail usually varies as an inverse power of the distance x from the surface.

$$n_S(x) = fJ_0\tau\frac{r+1}{d}\left(\frac{d}{x-l+d}\right)^{2+r}. \tag{31}$$

In particular, (31) is valid for the *I-I-B* model with $r=r_I$ defined in (27) and $d=d_I$ given by (30) or (25). When $R=0$ in the *V-I-B* model, (31) is valid with $r=r_0$ defined in (15) and $d=d_0$ given by (23) or (13). In Appendix A, it is shown that conservation of particles usually makes $R=0$. In certain cases (e.g., $R\cong 1$ in the *V-I-B* model) n_S may have the exponential form (22).

(*b*) *The exponent* $2+r$ in (31) is independent of E, J_0, and τ, but depends on T in general, since the diffusion coefficients are temperature-dependent [see Eqs. (15) and (27)]. Thus, $2+r$ is the most significant parameter obtained from experiments. A rough guide to the size of r can be obtained from the model for the combination constants given in Appendix B. Notice that for the *V-I-B* model, (15) gives $r_0=2$ for $D_I=D_V$ and $\beta_{VB}=\beta_{VI}$; for the *I-I-B* model, (27) gives $r_I=2$ for $D_I=D_B$ and $\beta_{IB}=\beta_{II}$. These results are reasonable since the B's and I's are indistinguishable in these limiting cases, and the I profiles are inverse-square law.

In order to obtain rough estimates of the order of magnitude of r, we set $\rho_{VI}=\rho_{VB}$, $z_V=z_I=z_B$, $a_V=a_I=a_B$, and $N_V=N_I=N_B$ in (43) and $\rho_{II}=\rho_{IB}$ and and $a_I=a_B$ in (44). This gives

$$r_0(r_0+1) = 6\frac{D_I}{D_B}\frac{D_V+D_B}{D_V+D_I}, \quad r_I(r_I+1) = 3\left(1+\frac{D_I}{D_B}\right). \tag{32}$$

Some interesting limiting cases of (32) are

$$r_0 \ll 1 \quad \text{for} \quad D_I \ll D_B \ll D_V \tag{33}$$

$$\cong (6D_I/D_B)^{1/2} \quad \text{for} \quad D_B < D_I \ll D_V \tag{34}$$

$$\cong 2 \quad \text{for} \quad D_V \ll D_B, \quad D_V \ll D_I; \tag{35}$$

$$r_I \cong 1.3 \quad \text{for} \quad D_I \ll D_B \tag{36}$$

$$\cong (3D_I/D_B)^{1/2} \quad \text{for} \quad D_B \ll D_I. \tag{37}$$

Thus, if $D_I \leqq 10D_B$, the range of r is $0 < r \leqq 7.7$.

(*c*) *The displacement* d in (31) is somewhat more dependent on the details of the models than are the form of the supertails and behavior of r. However, d should vary only very slightly with E and J_0, as discussed in Sec. 3. Since d-l can be determined fairly accurately in careful measurement of n_S for several orders of magnitude of change in n_S, the E and J_0 dependence of d should provide an additional test of the validity of the theory.

The orders of magnitude of the theoretical values of d are in agreement with the observed values. For example, with $D_I = 10^{-11}$ cm² sec⁻¹, $J_I(l) = 10^3 \times 10^{13}$ cm²/10³ sec, $z_I = 6$, $a_I = 4\times 10^{-8}$ cm, and $\rho_{II} = 1$; (30) and (41) give $d_I \cong 0.1\ \mu$.

(*d*) *The total number of ions in the supertail*, $N_{\text{tot}} = fJ_0\tau$, may not be exactly proportional to the total dose $J_0\tau$, because the fraction f of interstitial bombardants B which leave the generation region will depend on the number which combine with vacancies and interstitials in the generation region, and this number will depend on the number of vacancies and interstitials in the generation region, which in turn depends on the dose *rate* J_0 (and on the energy E). For the case suggested by Davies and Jespersgard[4] in which the only ions which get into the supertail are those which stop interstitially at the end of a channeling track, the situation is entirely different. Then N_{tot} probably *will* be proportional to the total dose $J_0\tau$, because the number of V's, I's, and B's at the end of the channeling is expected to be small enough that the effect of one well-channeled ion on another can be neglected.

The form of the supertail and the dependence of r on E, J_0, τ, and T are the "cleanest" theoretical results. In addition to these results and to the results (c) for d and (d) for N_{tot}, the following effect should also be mentioned:

(*e*) *Post annealing* an irradiated sample should have little effect on the supertail unless the annealing temperature is too high. Long-time annealing at very high temperatures should of course change the profile.

5. COMPARISON WITH EXPERIMENTS

Bower, Baron, Mayer, and Marsh[7] implanted 20-keV Sb ions into Si at 500°C and found that n_S had the power-law form (31) with $r \cong 0.2$ for over four orders of magnitude change of n_S and for $0 < x < 10\ \mu$. Lowering the implantation temperature from 500 to 300°C had little effect on the profile, but lowering the implantation temperature to 25°C reduced the concentration in the supertail. A post anneal for 10 min at 970°K had no effect on the profile, as expected.

These results admit to several reasonable interpretations. For the V-I-B model, the value of $r \cong 0.2$ is quite reasonable according to (33). The I-I-B model also explains the results. In either case, the insensitivity of r to lowering the implantation temperature is reasonable, since lowering the temperature changes $r+2$ from 2.2 to a value near 2.0, and this small change cannot be detected within experimental error. Furthermore, the electrically active defects in the supertail may not be Sb ions. For example, they could be trapped I's or trapped V's; in either case, we expect $\eta = 2$, which is within the accuracy of determining η. Alternatively, the fairly large C impurity concentration in the implanted beam could cause the supertail.

The validity of the capacity method used to measure these profiles has been questioned.[27] However, Meyer[8] has recently confirmed the results of Bower *et al.*[7] by an independent method. The fact that the supertail was reduced by implanting at 25°C is further evidence that the observed profile is not caused entirely by the method of measurement, since the same method was used to observe both the high- and low-temperature profiles.

Davies and Jespersgard[4] found that injecting 20-keV Xe ions into W at room temperature gave a supertail, as shown in Fig. 1, where the points from the experimental curve gave a very good fit to the solid theoretical curve $\sim (x - l + d_0)^{-5.7}$, with $d_0 - l = 2$ mg/cm² $= 1\ \mu$. The poor fit to an exponential, which results from the single-stream diffusion model,[4] is shown for comparison. Since the residual activity is the integral of the remaining n_S's, this gives $n_S \sim (x - l + d_0)^{-6.7}$; thus, $r = 4.7$. Since

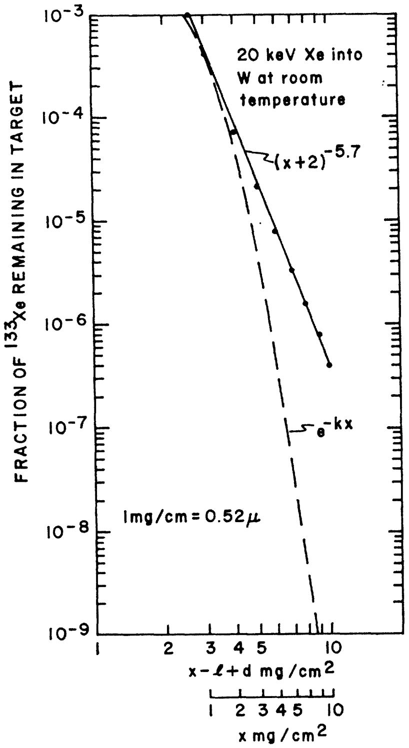

FIG. 1. Integral penetration distribution for 20-keV Xe into W at room temperature. The points are replotted from the experimental curve of Davies and Jespersgard (Fig. 3 of Ref. 4), and the theoretical solid curve is $\sim (x+2)^{-5.7}$.

---

[27] D. P. Kennedy, P. C. Murley, and W. Kleinfelder, Electrochemical Society Meeting, Boston, Mass. 1968 (unpublished).

vacancies in W are usually considered to be immobile at room temperature,[28] while interstitials are considered to be quite mobile, these supertails in W probably result from the *I-I-B* diffusion. However, the *V-I-B* model cannot be ruled out conclusively, as pointed out by McCaldin,[15] since the usual static measurements of the vacancy-diffusion coefficient could be controlled by trapped vacancies, while the present process involves free vacancies.

Kornelsen, Brown, Davies, Domeij, and Piercy[3] found that bombarding 40-keV Xe into W at room temperature gave a supertail almost identical with the 20-keV curve of Fig. 1. A log-log plot of the $\langle 100\rangle$ curve of Fig. 14 of Ref. 3 gives a close fit to the theoretical curve $\sim(x-l+d)^{-5.9}$, with $d-l=2$ mg/cm^2$=1.04$ μ for three orders of magnitude change of concentration, as shown in Fig. 2. The difference between $2+r=6.7$ and 6.9 for 40- and 20-keV ions, respectively, is within the accuracy of replotting the published curves. The insensitivity of $2+r$ and of d to a factor of 2 change in energy is in agreement with the theory, as discussed in (b) and (c) in Sec. 4. The insensitivity of the *shape* of the tails to surface treatment (Figs. 12 and 13 of Ref. 3) is in agreement with the theory, since the major effect of changing the surface condition in this experiment is to reduce the number of channeled ions, which is believed to reduce the number of interstitial bombardants.

Herrmann, Lutz, and Sizmann[6] irradiated a single-crystal W sample with a beam of 50-keV Kr ions making an angle of 7.5° with a $\langle 111\rangle$ axis at 78°K, and heated the sample to room temperature before measuring the concentration profile. The concentration dropped off much more slowly with the distance from the surface than that of a similar implantation at room temperature. It appears that the Kr ions are immobile at 78°K, but become mobile and diffuse as the temperature is raised. Since it is unlikely that the Kr ions, self-interstitials, and vacancies become mobile at the same temperature, there are no diffusing self-interstitials or vacancies to trap the diffusing Kr ions. Consequently, they penetrate deeper into the crystal.

An explanation of the results in terms of channeling would require that the Kr ions diffuse out of the supertail at 78°K as a result of the He$^+$ postbombardment. Since the Kr ions in the tail are immobile at room temperature, the He$^+$ bombardment would have to enhance the Kr diffusion coefficient by at least 10^8 (as a conservative estimate), which is unlikely. Also, the enhanced diffusion should cause *more* ions to appear in the supertail, since those in the stopping region should diffuse into the supertail region.

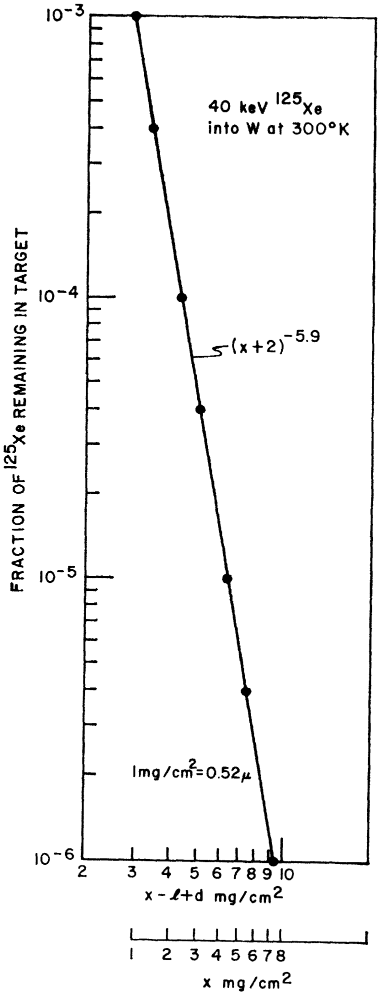

FIG. 2. Integral penetration distribution for 40-keV Xe in W. The points are replotted from the experimental curve of Kornelsen *et al.* (Fig. 14, Ref. 3), and the solid curve is the theoretical curve $\sim(x+2)^{-5.9}$.

Similar results were obtained for K ions implanted into W by Davies, Erikson, and Whitton[5] in a study of the maximum channeling range. Bombarding 40-keV K ions into W along $\langle 100\rangle$ at 300°K gave a supertail past the maximum channeling range which decayed for a little over two orders of magnitude of change in n_S as a power law with $2+r\cong3$ and d-$l\cong0.15$ μ, as shown in Fig. 3. Bombarding at 30°K, heating to room temperature, and then measuring the profile gave a more deeply penetrating profile, as in the experiment of Herrmann and co-workers.[6]

Dearnaley, Freeman, Gard, and Wilkins[21] implanted 5×10^{12} ^{32}P ions per cm^3, at 12 and 40 keV into Si at room temperature, with the channeling suppressed by implanting along nonchanneling direction or by implanting large doses of ^{31}P+^{32}P. The curve for an

---

[28] G. H. Kinchin and M. W. Thompson, J. Nucl. Energy **6**, 275 (1958); M. W. Thompson, Phil. Mag. **5**, 278 (1960); V. H. Schultz, Z. Naturforsch. **14A**, 361 (1959); H. Schultz, in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill *et al.* (Academic Press Inc., New York, 1965), p. 761; R. A. Johnson, *ibid.*, p. 582; Y. A. Kraftmakhev and P. G. Strelkov, Fiz. Tverd. Tela **4**, 2271 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1662 (1963)]; G. D. Watkins, in *Radiation Damage in Semiconductors*, edited by P. Baruch (Academic Press Inc., New York, 1964), p. 103.

implantation at 8° to a ⟨110⟩ axis is shown in Fig. 4. The experimental points fit the theoretical curve $\sim(x-x_0)^{-\eta}$, with $x_0 \cong 0.05$ μ and $\eta=5.6$, fairly well. The accuracy of determining η and x_0 is poor because the tail is short. The curve for the 12-keV ions (Fig. 5 of Ref. 21) is even shorter, but a log-log plot does give a straight line with $\sim 4<\eta<\sim 8.5$, which is consistent with $\eta \cong 5.6$ for the 40-keV ions.

Kleinfelder, Johnson, and Gibbons[22] implanted 3×10^{15} K ions per cm², at 30 and 50 keV into Si, approximately along a ⟨111⟩ axis at 625°C. The concentration n_S decayed exponentially for over five orders of magnitude of change in n_S, extending from ~ 0.1 to ~ 0.4 μ for the 30-keV ions, and from ~ 0.2 to 0.55 μ for the 50-keV ions. The decay constants were $k_B = 225$ Å^{-1} and $k_B = 297$ Å^{-1} for the 30- and 50-keV ions, respectively. This gives $k_B \sim \sqrt{E}$.

These long exponential decays could result from channeling with a probability for dechanneling which is a constant along the channeling path.[29] The difficulties with this interpretation are that the constant dechanneling probability over such a large range and the energy dependence of k have not been explained. Multistream diffusion offers an alternative explanation. The very large dose of 3×10^{15} ion per cm² could cause sufficient damage in the stopping region to upset the balance of I's and V's, causing R to differ from zero in the V-I-B model. From (24), $k_B \sim [n_V(l)]^{1/2}$, and it is possible that $n_V(l) \sim E$ is approximately satisfied, since the naive model—that the number of vacancies created is equal to the energy E divided by the energy necessary to create a vacancy—gives $n_V(l) \sim E$. Thus $k_B \sim \sqrt{E}$, in agreement with experiment. The difficulties with the diffusion explanation are that the supertail lies well within the maximum channeling range under ideal conditions, that there has been no verification that the ions diffuse into the supertail in this experiment, and that the theory has not been developed in detail for this case.

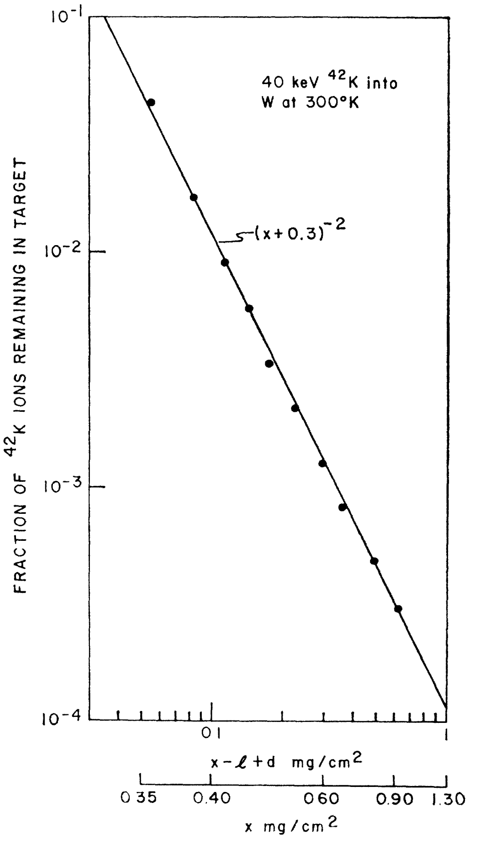

FIG. 3. Integral penetration distribution for 40-keV ^{42}K into W at 300°K. The experimental points are from Davies, Eriksson, and Whitton,[6] and the theoretical curve is $\sim(x+0.3)^{-2}$.

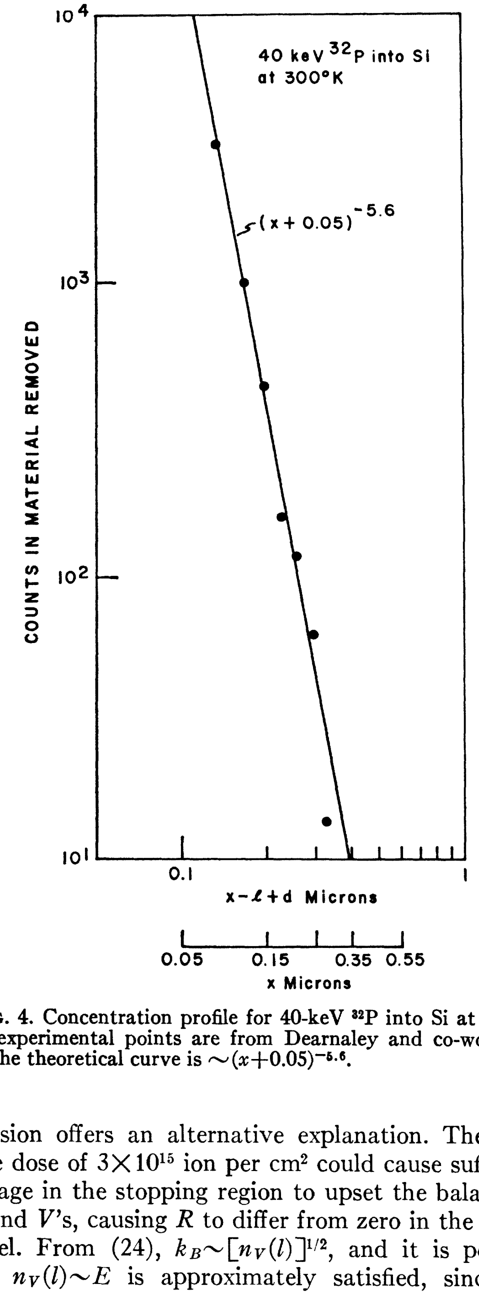

FIG. 4. Concentration profile for 40-keV ^{32}P into Si at 300°K. The experimental points are from Dearnaley and co-workers,[21] and the theoretical curve is $\sim(x+0.05)^{-5.6}$.

The results of two other experiments may also be related to multistream diffusion. First, the *integral*

---

[29] J. Gibbons (private communication).

concentration profiles for both 5-keV ^{133}Xe and 5-keV ^{85}Kr ions injected into polycrystalline W from Fig. 2 of Ref. 3 give quite a good fit to the theoretical curve $\sim(x-l+d)^{-3.0}$, with $d-l=0.01$ mg/cm^2. Although the reason for $r=2$ in these cases is not understood, it is interesting to note that this value of r can arise in one of several ways: (i) The *B-B* model gives $r=2$, (ii) $r=2$ if $\rho_{VB}=\rho_{VI}$ and $\beta_{VB}=\beta_{VI}$ in the *V-I-B* model, and (iii) $r=2$ if $D_I=D_B$ and $\beta_{IB}=\beta_{II}$ in the *I-I-B* model. It should be mentioned that for the polycrystalline samples the power-law profiles extend up to the surface of the sample.

Second, the theory may have implications concerning vacancy-enhanced diffusion experiments,[16,17] which have been interpreted as a creation near the surface of vacancies, which diffuse to the edge of a prediffusion profile (at 10 μ) and cause the substitutional impurities to diffuse more rapidly. An alternative explanation is that the protons may knock some of the substitutional impurities into interstitial sites, where they can diffuse according to the present theory.

ACKNOWLEDGMENTS

Discussions with R. Baron, R. W. Bower, R. Kikuchi, R. Mankarious, O. J. Marsh, J. Mayer, J. O. McCaldin, G. Picus, and G. Shifrin were invaluable in formulating the theory. The author gratefully acknowledges stimulating conversations with R. De Wames, J. Gibbons, J. Moll, G. Pearson, and W. G. Wagner. J. O. McCaldin discussed his unpublished work freely. A. Seeger made valuable suggestions on the manuscript. I also would like to thank Dr. G. F. Smith and Dr. J. M. Richardson for the hospitality of the Hughes Research Laboratories during the summer of 1966.

APPENDIX A: VALUE OF R IN *V-I-B* MODEL

There are several ways to show that conservation of particles requires that R [defined in Eq. (7)] be much smaller than unity. Perhaps the easiest way is to integrate n_V and n_I in Eq. (12) from $x=0$ to $x=L$. Equating the results gives

$$\frac{R}{1-R}=\frac{d_0}{L}\left(\frac{D_V}{D_I}+1\right), \tag{38}$$

when $L\gg d_0$. In the limit $L\to\infty$, in which case the two integrals give the total numbers N_V and N_I of V's and I's, respectively, (38) gives $R=0$. The essential feature of this and the other arguments for $R=0$ is that if $R\neq0$, then N_V and N_I cannot be equal because N_V will be infinite while N_I is finite, or vice versa.

APPENDIX B: MODEL FOR COMBINATION COEFFICIENTS

For a unit box containing one V and one I, we want the probability β_{VI} per unit time that the I and B will combine to make a *V-I* pair. Assuming the simplest model[30] for the diffusion process gives D_V/a_V^2 for the number of jumps per second made by the vacancy, where a_V is the vacancy jump distance. The probability per jump that the V lands on one of the z_V neighboring V sites of the I is z_V/N_V, where N_V is the number of V sites in the unit box. With the corresponding expressions for the I's, the probability per second that the V and I will land on neighboring sites, multiplied by the probability ρ_{VI} that they will then combine, is

$$\beta_{VI}=\left(\frac{z_VD_V}{a_V^2N_V}+\frac{z_ID_I}{a_I^2N_I}\right)\rho_{VI}. \tag{39}$$

The corresponding expressions for the other β's are

$$\beta_{VB}=\left(\frac{z_VD_V}{a_V^2N_V}+\frac{z_BD_B}{a_B^2N_B}\right)\rho_{VB}, \quad \beta_{VV}=\frac{z_V\rho_{VV}}{a_V^2N_V}2D_V, \tag{40}$$

$$\beta_{IB}=\frac{z_I\rho_{BI}}{N_I}\left(\frac{D_I}{a_I^2}+\frac{D_B}{a_B^2}\right), \quad \beta_{II}=\frac{z_I\rho_{II}}{a_I^2N_I}2D_I. \tag{41}$$

The rate of change of n_V from the *V-I* process is the probability per second β_{VI} that a pair will combine multiplied by the number n_Vn_I of *V-I* pairs: $dn_V/dt=\beta_{VI}n_Vn_I$. Similarly, for the *I-I* process $dn_I/dt=2\beta_{II}\times\frac{1}{2}n_I(n_I-1)\cong\beta_{II}n_I^2$, where $\frac{1}{2}n_I(n_I-1)$ is the number of I pairs and a factor of 2 is included because each *I-I* pair which is formed reduces n_I by 2.

Although this model for the β's is obviously quite crude, it should be useful for estimating the order of magnitudes of the sizes of the β's and the effects of changing such parameters as T, ion size, etc. For instance, the effect of the strain field around a large interstitial can be represented by using effective values ρ and z. For rough estimates, (39) can be simplified by setting $z_I\cong z_V\equiv z$, $a_I\cong a_V\cong a$ (the lattice constant), and $N_V\cong N_I\cong a^{-3}$. This gives

$$\beta_{VI}\cong za\rho_{BI}(D_V+D_I). \tag{42}$$

With these expressions [(40)–(42)] for the β's, (15) and (27) become

$$r_0(r_0+1)=6\frac{\rho_{VB}D_I}{\rho_{VI}D_B}\,\frac{z_VD_V/a_V^2N_V+z_BD_B/a_B^2N_B}{z_VD_V/a_V^2N_V+z_ID_I/a_I^2N_I} \tag{43}$$

and

$$r_I(r_I+1)=3\frac{\rho_{IB}a_I^2}{\rho_{II}a_B^2}\left(1+\frac{D_Ia_B^2}{D_Ba_I^2}\right). \tag{44}$$

APPENDIX C: BUILDUP TO STEADY STATE

In this Appendix an estimate is made of the values of the diffusion coefficients required for the steady-state

---

[30] See, for example, C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley, J. H. Hollomon, R. Maurer, and F. Seitz (John Wiley & Sons, Inc., New York, 1952). More sophisticated treatments give the same result to within a constant of the order of unity.

assumption to be valid. The theory requires that the steady state be maintained during a large fraction of the bombarding time at the greatest depth x_g where the profile is measured. In order to calculate the values of diffusion coefficients required to establish this steady state, the solution of the diffusion equations including the time dependence must be known. But these equations have not been solved. An upper limit on the diffusion constant could be obtained by requiring the diffusion of the V's, I's, and B's in the V-I-B model (or the I's and B's in the I-I-B model, or the V's and B's in the V-V-B model) to reach the steady state at $x \cong x_g$ and $t \cong \frac{1}{2}\tau$ in the absence of any trapping. This gives roughly $\exp(-x_g^2/2D\tau) \gtrsim 0.9$ or $x_g^2/2D\tau \lesssim 0.1$, which means

$$D \gtrsim x_g^2/0.2\tau. \tag{45}$$

A better estimate should be that the diffusion in the absence of trapping must establish a concentration $n_S(x_g)$ at $x \cong x_g$ in a time $t \cong \frac{1}{2}\tau$; that is,

$$n_S(l)\exp(-x_g^2/2D\tau) \gtrsim n_S(x_g), \tag{46}$$

which gives

$$D \gtrsim \frac{x_g^2}{2\tau \ln[n_S(l)/n_S(x_g)]}. \tag{47}$$

Some confidence in this approximation can be gained by checking it for a problem which can be solved exactly. For ions diffusing and being trapped by a fixed number of trapping centers, the diffusion equation

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} - \omega n$$

can be solved exactly by taking the Laplace transform in time. For $x_g > (D/\omega)^{1/2}$, the condition that $n(x_g)$ reach 90% of its steady-state value in a time $t \cong \frac{1}{2}\tau$ is just (47).

For the inverse-power profile, (47) gives (with $\eta \equiv 2+r$)

$$D \gtrsim \frac{x_g^2}{2\tau\eta \ln[(x_g - l + d_0)/d_0]}. \tag{48}$$

For the typical values $x_g \cong x_g - l + d_0 = 3\ \mu$, $\tau = 300$ sec, $\eta = 7$, and $d_0 = 1\ \mu$, (48) gives $D \gtrsim 10^{-10}$ cm^2 sec^{-1}.

Diffusion coefficients for interstitial ions in Si are equal to 10^{-9} cm^2 sec^{-1} at temperatures of 660, 570, 1270, 650, and 940°K for Cu, Li, Ag, Fe, and Au, respectively.[31] The vacancy-diffusion coefficient is difficult to measure, but Watkins[32] estimated the jump frequency ν to be $2\times10^{12}\exp(-U/k_BT)$, with $U = 0.33 \mp 0.03$ eV. With $D_V \cong a^2\nu$, this gives $D_V = 10^{-9}$ cm^2 sec^{-1} at 250°K, and at 77°K, $D_V \cong 3\times10^{-5}$ cm^2 sec^{-1}. This suggests that the vacancies move much faster than interstitials in Si.

---

[31] B. J. Boltaks, *Diffusion in Semiconductors* (Academic Press Inc., New York, 1963).

[32] G. D. Watkins, J. Phys. Soc. Japan **18**, Suppl. II, 22 (1963); also see G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. **31**, 86 (1961).