with pyrex tubing around the ruby rod indicates that Flowers and Jenney are, in fact, correct.

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Diffusion with Interstitial-Substitutional Equilibrium. Zinc in GaAs

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The diffusion of an impurity existing in a substitutional-interstitial equilibrium in an extrinsic semiconductor is considered. The dependence of the effective diffusion coefficient D on the impurity concentration can be simplified by assuming that the concentrations of the substitutional species and electrical carriers are nearly equal and that the diffusion of the substitutional species can be neglected. Then D is shown to vary as the first, second, or third power of the impurity concentration depending on the charge states of the substitutional and interstitial species. Universal calculated results are presented for these three cases for a constant surface concentration and semi-infinite medium. The results are used to explain the anomalous diffusion of zinc in GaAs, for which the model predicts that D should vary as the square of the concentration. Six available diffusion profiles at 1000°C can be fit using a single parameter, and the small temperature dependence of available diffusion profiles is in accordance with the theory. The interstitial zinc concentration is estimated to be several orders of magnitude below that of the substitutional zinc.

I. INTRODUCTION

THE diffusion of zinc in many semiconductors is frequently unusual. For example, although it diffuses substitutionally in germanium,[1] it diffuses interstitially in silicon.[2] There are conflicting reports of zinc diffusion in InSb,[3–4] and in GaP, zinc diffusion is concentration dependent.[6,7]

The case studied most fully is that of zinc diffusion in GaAs. Here it was found that the diffusion is rapid, the diffusion front is anomalously sharp, and the diffusion profile depends on the surface concentration of zinc.[8–11] The first attempt to explain this behavior was made by Allen,[12] who proposed that the zinc diffuses in both a neutral and ionized state. However, Goldstein soon refuted this explanation by pointing out that the zinc forms an impurity band merging with the valence band,[9] and, furthermore, demonstrated that within an experimental error of 10%, all the zinc is ionized.[13] Next, Kendall and Jones[11] advanced the suggestion that the zinc diffuses substitutionally but is enhanced due to an increase in the gallium vacancy concentration. However, they have not yet published a quantitative fit to the data. More recently, Longini[14] has suggested that zinc can exist as an interstitial species at high zinc concentrations, and thereby dominate the diffusion process. However, Longini only provided plausibility arguments for this explanation, with no quantitative treatment of the diffusion problem.

In the present work, the problem of the diffusion of a species in interstitial-substitutional equilibrium is shown to be reducible to a concentration-dependent diffusion process, by applying several appropriate restrictions. General solutions are presented for diffusion profiles for the cases when the diffusion constant varies as the first, second, and third power of the concentration. The results are shown to provide a good quantitative fit to data of zinc diffusion in GaAs.

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[14] R. L. Longini, Solid-State Electron. **5**, 127 (1962).

II. SUBSTITUTIONAL-INTERSTITIAL EQUILIBRIUM DIFFUSION

There are three cases considered, depending on whether there is a net difference of one, two, or three electrical charges between the interstitial and substitutional species. These are referred to as cases (a), (b), and (c), respectively. A typical example of these three cases is where the substitutional species is a single acceptor, and the interstitial species is either (a) neutral, (b) a single donor, or (c) a double donor.

It will be assumed in the following that vacancy equilibrium is always maintained. In an intrinsic semiconductor, simple application of the mass-action principle provides the following equations for the three cases, respectively:

$$K_a = n_i (N_s/N_i)_{\text{intr}}, \tag{1a}$$

$$K_b = n_i^2 (N_s/N_i)_{\text{intr}}, \tag{1b}$$

$$K_c = n_i^3 (N_s/N_i)_{\text{intr}}. \tag{1c}$$

Such relations have been previously applied to the case of copper in germanium,[15] and are of interest here only to evaluate the equilibrium constants, K_a, K_b, K_c. Here n_i is the intrinsic electron concentration, N_i the interstitial concentration, the subscript "intr" refers to the quantity in intrinsic material, and N_s is the substitutional concentration. It is shown in the Appendix that Eqs. (1) [and also Eq. (2) below] apply even if the presence of charged vacancies is included.

In extrinsic material, assuming that $p \approx N_s$ (i.e., $N_s \gg N_i$), where p is the concentration of holes (or electrons), and again applying the mass action principle for three cases:

$$N_i = N_s^2/K_a; \tag{2a}$$

$$N_i = N_s^3/K_b; \tag{2b}$$

$$N_i = N_s^4/K_c. \tag{2c}$$

For such a two-species diffusion process, Fick's law in one dimension is

$$\frac{\partial}{\partial x}\left(D_i \frac{\partial N_i}{\partial x} + D_s \frac{\partial N_s}{\partial x}\right) = \frac{\partial (N_i + N_s)}{\partial t}, \tag{3}$$

where D_i and D_s are, respectively, the interstitial and substitutional diffusion coefficients. Substituting Eqs. (2) into Eq. (3), and realizing that $N_i \ll N_s$, Eq. (3) is reduced to a single-species diffusion equation with an effective diffusion coefficient, D, where D is defined by the general diffusion equation $(\partial/\partial x)(D\partial N_s/\partial x) = \partial N_s/\partial t$. Thus, for the three cases,

$$D = D_s + 2D_i N_s/K_a = D_s + 2D_i N_i/N_s; \tag{4a}$$

$$D = D_s + 3D_i N_s^2/K_b = D_s + 3D_i N_i/N_s; \tag{4b}$$

$$D = D_s + 4D_i N_s^3/K_c = D_s + 4D_i N_i/N_s. \tag{4c}$$

[15] C. Frank and F. D. Turnbull, Phys. Rev. **104**, 617 (1956).

To solve the diffusion equation, a separate solution is required for each temperature and surface concentration. However, universal solutions can be found if it is assumed that D_s can be neglected in Eqs. (4). Then expressing D in terms of the surface concentration N_{sur} and diffusion coefficient D_{sur} at the surface ($x=0$):

$$D = D_{\text{sur}}(N_s/N_{\text{sur}}); \tag{5a}$$

$$D = D_{\text{sur}}(N_s/N_{\text{sur}})^2; \tag{5b}$$

$$D = D_{\text{sur}}(N_s/N_{\text{sur}})^3. \tag{5c}$$

This reduces the problem to solving a concentration-dependent diffusion equation, which is readily accomplished for the case of constant surface concentration and a semi-infinite medium. Well-known mathematical manipulations were applied,[16] and computer solutions were employed.

The results for the three cases are given in Table I, and are shown in Fig. 1, in terms of the usual dimensionless quantities $C = (N_s/N_{\text{sur}})$ and $y = x/(4D_{\text{sur}}t)^{1/2}$. Also shown in Fig. 1 for comparison is the normal complementary error function solution for a constant diffusion coefficient. The solution to case (a) is essentially identical to that given by Crank.[16] It should be noted that, for the three cases, there is a finite value of y for which the value of C approaches very close to zero. It is also noteworthy that the diffusion profile for the three cases is not easily distinguished from a concentration-independent diffusion until $C < 0.5$.

TABLE I. Solutions to diffusion equation for a constant surface concentration and semi-infinite medium, for the three cases where the diffusion constant depends on the first, second, and third power of the concentration (shown in Fig. 1). Here, $C = N_s/N_{\text{sur}}$ and $y = x/(4D_{\text{sur}}t)^{1/2}$.

	C for case				C for case	
y	(a)	(b)	(c)	y	(a)	(b)
0.001	0.999	0.999	0.999	0.46	0.503	0.425
0.005	0.996	0.996	0.997	0.48	0.477	0.373
0.01	0.991	0.992	0.993	0.50	0.451	0.312
0.02	0.982	0.985	0.986	0.52	0.425	0.234
0.05	0.955	0.961	0.964	0.54	0.398	0.107
0.10	0.907	0.918	0.925	0.545		0.022
0.15	0.858	0.872	0.881	0.546		0.000
0.20	0.807	0.822	0.830	0.56	0.370	
0.25	0.753	0.766	0.769	0.58	0.343	
0.30	0.697	0.703	0.697	0.60	0.315	
0.32	0.674	0.677	0.663	0.62	0.287	
0.34	0.650	0.648	0.624	0.64	0.258	
0.36	0.626	0.617	0.577	0.66	0.229	
0.38	0.602	0.584	0.521	0.68	0.199	
0.40	0.578	0.550	0.449	0.70	0.169	
0.42	0.553	0.512	0.340	0.72	0.139	
0.43			0.237	0.74	0.108	
0.435			0.058	0.76	0.077	
0.436			0.000	0.78	0.045	
0.44	0.528	0.471		0.80	0.013	
				0.808	0.000	

[16] J. Crank, *The Mathematics of Diffusion* (Oxford University Press, London, 1956), p. 165.

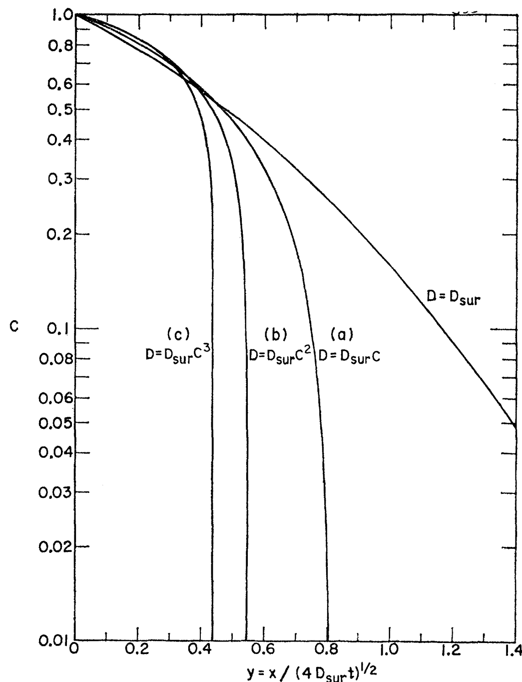

FIG. 1. Solutions to diffusion equation for a constant surface concentration and semi-infinite medium for the three cases where the diffusion coefficient depends on the first, second, and third power of the concentration (data given in Table I), and also for an invariant diffusion coefficient. Here $C = N_s/N_{sur}$ and $y = x/(4D_{sur}t)^{1/2}$.

III. ZINC DIFFUSION IN GaAs

Before applying the above solutions to the case of zinc in GaAs, it is necessary to examine the applicability of the above restrictions. The assumption that $p \approx N_s$ is in accordance with Goldstein's finding[13] that, within experimental error, there is a one-to-one correspondence between the zinc and hole concentrations. The assumption that vacancy equilibrium is always maintained should apply at the highest temperatures since diffusion times as long as 10^4 sec are typically used, and GaAs usually contains at least 10^4 dislocations cm^{-2}. This is in contrast to copper diffusion in GaAs,[17,18] which diffuses orders of magnitude faster than zinc, and, hence, is limited by vacancy formation. In the absence of suitable data, no *a priori* justification can be given for neglecting D_s in Eq. (4). Such justification will be provided by demonstrating that the theory fits the data adequately.

The question next arises as to whether interstitial zinc is a single or double donor. The second ionization potential (in vacuum) of zinc (17.9 eV) exceeds the first potential for hydrogen (13.5 eV), and is close to the second ionization potential for copper (20.3 eV).[19] Since in GaAs hydrogen is neutral,[20] while interstitial copper is a single donor,[18] it is concluded that interstitial zinc is most probably a single donor. Since zinc is a single acceptor in GaAs, case (b) of the above diffusion results should apply to zinc diffusion.

In Fig. 2 is shown the agreement between experiment and theory. The experimental data shown are those of Cunnell and Gooch[8] from their Fig. 3(b), which exhibits the most complete data. It can be seen that the fit is satisfactory except at the lowest zinc concentrations, where the computed zinc concentration is too low. This behavior is to be expected because of the approximation made in reducing Eqs. (4) and (5). At the lowest values of N_s, D_s cannot be neglected, so

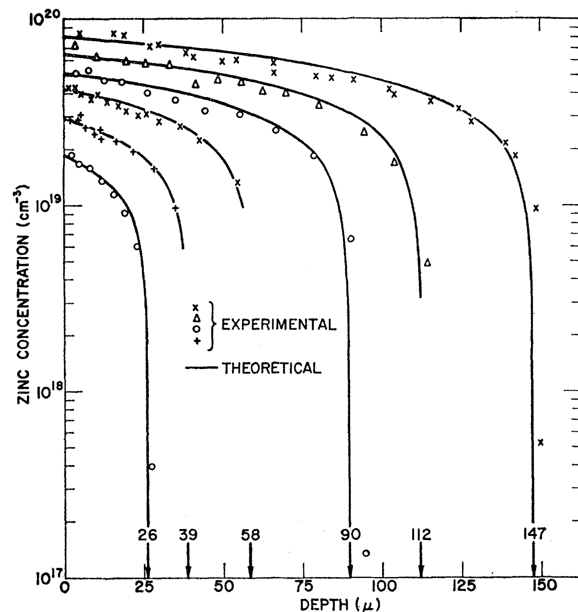

FIG. 2. Experimental and theoretical variation of zinc concentration with distance at 1000°C in GaAs. The experimental data are those of Cunnell and Gooch (Ref. 8). The arrows indicate the "effective zero" for each theoretical curve.

that the solution at low concentrations should tend to a concentration-independent diffusion and be less steep. In addition, at the lowest concentration, the GaAs starts to become intrinsic, since at 1000°C, $n_i \approx 7 \times 10^{17}$ cm^{-3}. This will also cause the diffusion profile to revert to that of normal diffusion. It is to be noted that the diffusion profiles could not be fit by assuming case (a) or (c) to apply. Although not explicitly mentioned, the analysis shown in Fig. 5 of Cunnell and Gooch[8] indicates

[17] C. S. Fuller and J. M. Whelan, J. Phys. Chem. Solids **6**, 173 (1958).

[18] R. N. Hall and J. H. Racette, Bull. Am. Phys. Soc. **7**, 234 (1962).

[19] See, for example, *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1956), 38th ed., p. 2347.

[20] L. R. Weisberg, F. D. Rosi, and P. G. Herkart, in *Properties of Elemental and Compound Semiconductors*, edited by H. C. Gatos (Interscience Publishers, Inc., New York, 1960), p. 25.

that the effective diffusion constant varies roughly as the square of the zinc concentration, in agreement with the results of Fig. 2.

Another check on the theory is that according to Eqs. (4b) and (1b), with D_s neglected, at $x=0$

$$D_{\text{sur}}=3D_iN_{\text{sur}}^2/K_b=(3D_iN_{\text{sur}}^2/n_i^2)(N_i/N_s)_{\text{intr}}. \quad (6)$$

Thus, D_{sur} should vary as N_{sur}^2, and this variation is shown in Fig. 3. The value of D_{sur} is conveniently found from the "effective zero" intercepts indicated for the curves in Fig. 2, but can be obtained for any chosen value of y. Considering that each curve of Fig. 2 is fitted independently, the fit shown in Fig. 3 is again satisfactory. It is also realized that the results of Fig. 3 imply that all six curves of Fig. 2 can be fit by a single adjustable parameter.

A value of $(N_i/N_s)_{\text{intr}}$ can be estimated from Fig. 3 by application of Eq. (6). The slope of the line is

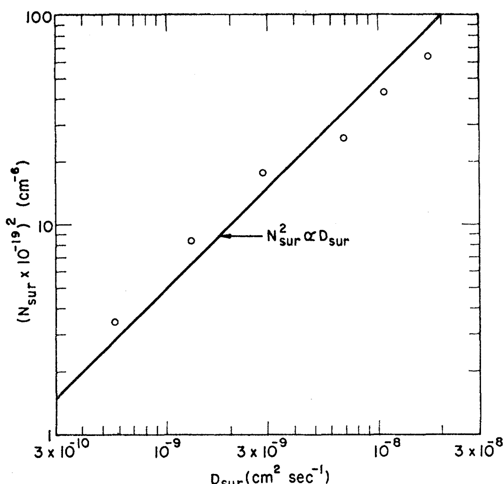

FIG. 3. The variation of N_{sur} with computed D_{sur} for zinc diffusion in GaAs at 1000°C.

5×10^{47} cm^{-8} sec, $n_i=7\times10^{17}$ cm^{-3}, and D_i is assumed to be 4×10^{-5} cm^2 sec^{-1} (compared to an extrapolated value[18] for interstitial copper at 1000°C of 4×10^{-4} cm^2 sec^{-1}). It is found that $(N_i/N_s)_{\text{intr}}=7\times10^{-9}$ so that, in intrinsic material, the concentration of interstitial zinc is negligible. However, since (N_i/N_s) increases as the square of the hole concentration, for 7×10^{19} zinc atoms cm^{-3}, $(N_i/N_s)=7\times10^{-5}$. Note, however, that the exact value of D_i chosen here is not crucial, since only the product $D_i(N_i/N_s)$ is of experimental significance.

Yet another check on the theory is provided by the temperature variation of the diffusion process. If controlled by the diffusion of substitutional zinc, the effective diffusion constant D would vary by nearly three orders of magnitude in the range 800 to 1100°C.[9] However, if interstitial diffusion predominates, according to Eqs. (1b) and (4b), D will vary with temperature as $\exp[-(E_{ID}+E_I-E_G)/kT]$, where E_{ID} is the activation energy for interstitial diffusion, E_I is the formation energy for interstitials, and E_G is the band-gap energy at 0°K. Since E_{ID} is typically about 0.5 eV,[18] and E_G is 1.6 eV for GaAs, then unless E_I appreciably exceeds 2 eV, D should vary by only one order of magnitude or less between 800 and 1100°C. The expected small temperature dependence of the diffusion profiles for nearly constant surface concentration of zinc[8,9,13] is shown in Fig. 4. The lack of a strong temperature dependence of the diffusion, together with the results of Figs. 2 and 3, provide strong *a posteriori* justification for neglecting D_s for this high-temperature zinc diffusion.

Actually, the assumption that D_s can be neglected breaks down under three conditions. As previously discussed, the first occurs when the total zinc concentration is low, such as at the diffusion front. The second condition exists when n_i becomes appreciable. This occurs for temperatures of 1100°C and above, where $n_i\geq1.5\times10^{18}$ cm^{-3}, so that the theoretical curves should not fit at the diffusion front. The third condition will prevail at lower temperatures when vacancy diffusion is sufficiently slow that vacancy equilibrium is not maintained. Then, even though there may be enough vacancies present so that substitutional diffusion is not affected, the interstitial concentration will be decreased since the substitutional concentration will not reach its equilibrium value. The curves will then tend to revert to well-behaved substitutional diffusion.

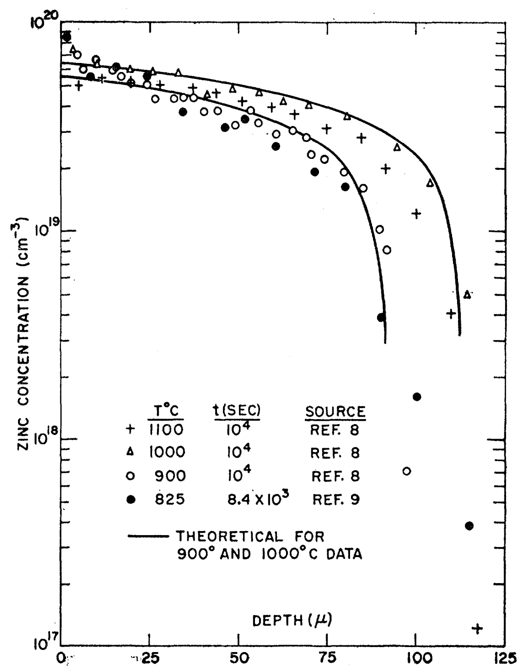

FIG. 4. The temperature variation of zinc diffusion profiles at nearly constant surface concentration.

The applicability of the first and third conditions may explain why Goldstein[9] observes an activation energy corresponding to substitutional diffusion. However, his results might still have been partially affected by interstitial diffusion, so that his value of D_0 may be somewhat too large. Evidence for this hypothesis is provided by the value of the effective diffusion constant of zinc at 1000°C, which has been found both here and elsewhere[8,11] to be as low as 6×10^{-10} cm^2 sec^{-1}. In contrast, Goldstein finds $D=2\times10^{-9}$ cm^2 sec^{-1} at 1000°C. In order to be able to neglect substitutional diffusion, this diffusion coefficient should be an order of magnitude lower.

IV. CONCLUSIONS

The general case of the diffusion of a species in interstitial-substitutional equilibrium is considered, and simplified under appropriate assumptions including the assumption that the interstitial species dominates the diffusion process. However, the concentration of the interstitial species varies as the second, third, or fourth power of the substitutional species, depending on the electronic states of the two species. The problem is thus reduced to a diffusion coefficient varying as the first, second, or third power of the concentration. This results in a diffusion profile that has a very sharp diffusion front.

The results of the theory are applied to the case of zinc diffusion in GaAs. Although interstitial zinc is present in only small concentrations, it dominates the diffusion process because of the high ratio of D_i/D_s. Since substitutional zinc is a single acceptor, and interstitial zinc is expected to be a single donor in GaAs, the diffusion coefficient should vary as the square of the concentration. It is shown that the six available diffusion profiles at 1000°C can be fit using a single adjustable parameter. There is no strong temperature variation observed of the diffusion profiles, which is suggestive of an interstitial diffusion process. Because of the excellent agreement between the data and the theory, it is concluded that the zinc diffusion between 800 and 1100°C is adequately explained as due to an interstitial-substitutional equilibrium.

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APPENDIX

The question arises as to whether Eqs. (1) and (2) will hold, in general, at equilibrium if the presence of N_v acceptor vacancies, v are taken into account. In general, the vacancies can be either neutral or charged, and an equilibrium exists

$$v^0 = v^{-r} + rh^+. \qquad (7)$$

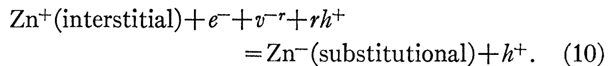
Then the equilibrium constant for this reaction is

$$K_1 = N_v p^r / N_v^0. \qquad (8)$$

Since the concentration of neutral vacancies is a constant independent of other defects at constant temperature and arsenic pressure, we can set

$$K_2 = N_v^0 K_1 = N_v p^r. \qquad (9)$$

The equilibrium reaction involving zinc atoms and vacancies can be expressed either in terms of charged or neutral vacancies. Here we choose to express the equilibrium in terms of charged vacancies, subject, of course, to Eq. (9). Using case (b) as an example,



$$\mathrm{Zn}^+(\text{interstitial}) + e^- + v^{-r} + rh^+ = \mathrm{Zn}^-(\text{substitutional}) + h^+. \qquad (10)$$

Equation (10) applies for both intrinsic and extrinsic material since Eq. (9) expresses the relation between charged and neutral vacancies. The equilibrium constant for Eq. (10) is:

$$K_3 = p^{2-r} N_s / N_i N_v. \qquad (11)$$

Thus,

$$K_2 K_3 = p^2 (N_s / N_i). \qquad (12)$$

Here, K_2K_3 implicitly contains the effect of neutral vacancies. By setting $K_2K_3 = K_b$, it is seen that Eqs. (1b) and (2b) follow directly since in the intrinsic case $p=n_i$ and for the extrinsic case $p=N_s$. Note that these two conditions imply that $N_v \ll n_i$ and N_s.