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# Anomalous Diffusion Profiles of Zinc in GaAs

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A number of workers investigating diffusion in semiconductors using radio-tracer techniques have reported a type of profile which is not easily explained by current theories of diffusion. This anomalous profile is usually found in experiments in which the solute concentration is high and has often been associated with the substitutional-interstitial diffusion mechanism. The profile shape is considered in this paper, taking the diffusion of zinc in GaAs at 1000°C as an example. The use of the Boltzman-Matano technique for analysing complex diffusion profiles is considered and experiments are described which suggest that the technique is not appropriate for this type of profile. An adaptation of the substitutional-interstitial diffusion theory is presented in which allowance is made for the possibility of the gallium vacancy concentration falling below the thermal equilibrium value. Theoretical profiles are computed and compared to experiments. Reasonable agreement is found.

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## 1. Introduction

A number of investigations which have plotted diffusion profiles of elements in semiconductors using radio-tracer techniques have produced anomalous profiles. One of the most frequently occurring anomalous shapes is a "double-profile" in which the curve appears to be made up of two shapes, one a shallow profile close to the surface and another deeper-penetrating one in the bulk. Such profiles are characterised by a region of decreasing slope giving rise to a concave region in the profile. Examples are shown in fig. 1 and fig. 2 due to the diffusion of zinc into InP and GaAs respectively. They have also been shown to occur at high solute concentrations for the diffusion of zinc in GaP [1], manganese in GaAs [2] and copper and nickel in Ge [3]. All of these are systems for which the substitutional-interstitial mechanism has been suggested as the principal diffusion mechanism.

When elements are diffused into solids from the vapour phase and the process can be described by a constant value of diffusion coefficient, then the measured profile is an error function complement curve. Other profile shapes indicate that the diffusion coefficient, $D$, is a function of concentration, $c$. The variation of $D$ with $c$ is commonly found from an experimentally determined profile using a graphical technique called the Boltzman-Matano method. This method involves selecting points along the diffusion profile and measuring the area under the graph and the slope at the point. Fig. 3 shows an analysis of the profile of fig. 2 obtained using this technique. Recent work on the diffusion coefficient of zinc in GaAs [4] by another method (isoconcentration technique) shows graphs of D versus $c$ which are quite different to fig. 3. It is also true that a simple application of substitutional-interstitial theory does not give rise to a variation of $D$ with $c$ such as that shown in the figure. One possible explanation which has been suggested [5] for this disagreement is that the Boltzman-Matano method of analysis is not valid for these systems. In this paper experiments are described which test the suggestion; the zinc/GaAs system is taken experimentally because of the large amount of data on the system. A non-equilibrium theory which has previously been suggested in a qualitative manner [6] is investigated and computer solutions are

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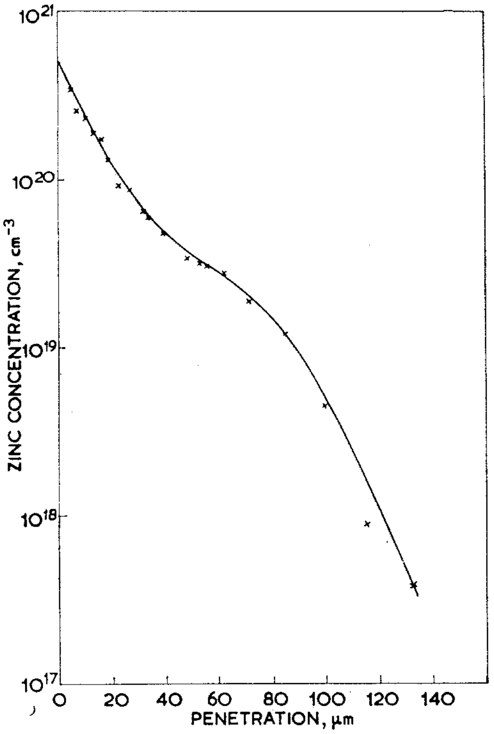

*Figure 1* Radio-tracer diffusion profile for zinc diffusing in InP at 800° C.

used to plot profiles which can then be compared to experimental ones.

## 2. Boltzman-Matano Analysis

This method may briefly be described as follows; it has been given in detail elsewhere [7]. For a diffusion coefficient which is concentration dependent, Fick's second law becomes:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D(c)\,\frac{\partial c}{\partial x}\right] \tag{1}$$

For any process which obeys a law of this form, it can be shown that the two variables $x$, $t$ can be replaced by a single variable, $\eta = x/\sqrt{t}$, providing the boundary conditions can also be expressed in terms of $\eta$ only. Substituting the variable $\eta$ into equation 1 we have:

$$\eta\,\frac{\mathrm{d}c}{\mathrm{d}\eta} = -\,2\,\frac{\mathrm{d}}{\mathrm{d}\eta}\left[D\,\frac{\mathrm{d}c}{\mathrm{d}\eta}\right] \tag{2}$$

which simplifies to

$$-\tfrac{1}{2}\int_{c=0}^{c=c'} \eta\,\mathrm{d}c = \left[D\,\frac{\mathrm{d}c}{\mathrm{d}\eta}\right]_{c=0}^{c=c'} \tag{3}$$

where $c'$ is some concentration on the profile.

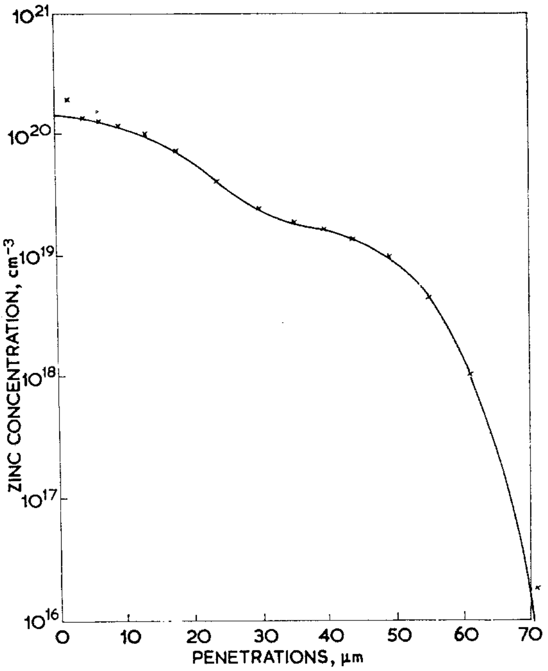

*Figure 2* Radio-tracer diffusion profile for zinc diffusing in GaAs at 1000° C.

Replacing $\eta$ with $x/\sqrt{t}$ we have an expression for the value of the diffusion coefficient at concentration $c'$

$$D(c') = -\,\frac{1}{2t}\left[\frac{\mathrm{d}x}{\mathrm{d}c}\right]_{c'}\int_0^{c'} x\,\mathrm{d}c \tag{4}$$

When impurities are diffused into semiconductors from the vapour phase the boundary conditions are:

(i) $c = 0$ for $x > 0$ at $t = 0$ and
(ii) $c = c_S'$ at $x = 0$ for $t > 0$

where $c_S'$ is the surface concentration, corresponding to the solubility of the diffusant in the semiconductor under the conditions of the experiment. The conditions can be expressed in terms of $\eta$ only:

(i) $c = 0$ for $\eta = \infty$ and
(ii) $c = c_S'$ for $\eta = 0$

and the Boltzman-Matano analysis is therefore valid providing equation 1 is obeyed. The experimental procedure therefore is to choose various concentrations $c'$ on an experimentally determined profile and measure the slope at the points and the areas under the profile. This gives the variation of $D$ with $c$.

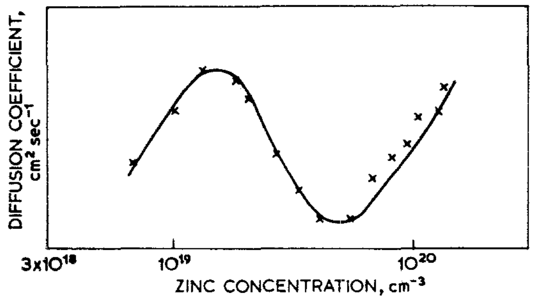

*Figure 3* Diffusion coefficient as a function of zinc concentration, derived from fig. 2 using Boltzman-Matano analysis.

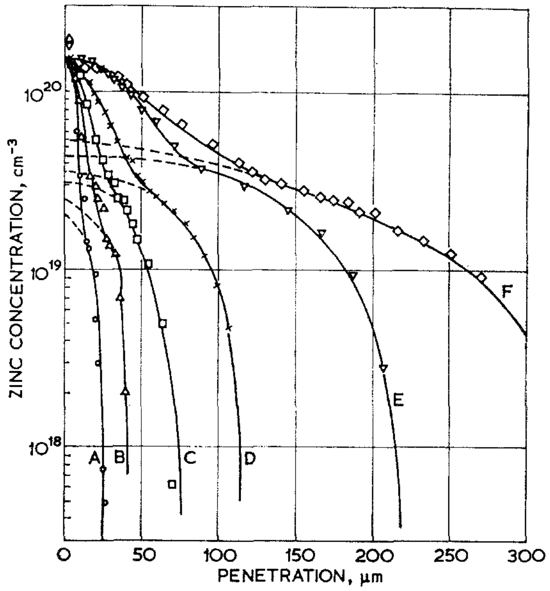

*Figure 4* Set of radio-tracer profiles for zinc in GaAs at 1000°C. Diffusion times were:

| | |
|---|---|
| Profile A | 10 min |
| ,, B | 30 min |
| ,, C | 90 min |
| ,, D | 3 h |
| ,, E | 9 h |
| ,, F | 30 h |

It may be seen that the validity of the analysis rests on the assumptions that it is permissible to replace the two variables, $x$, $t$, by the single variable $x/\sqrt{t}$; in other words it is assumed that the diffusion profile does not change its basic shape with time and progresses into the specimen as the square root of time. The assumption has been tested experimentally for the case of zinc in GaAs by Chang [8] and by Cunnell and Gooch [9] in the following way. A number of diffusions was carried out on pieces of GaAs all taken from the same slice. The samples were n-type, all with low donor doping $N_D$. The conditions for the diffusions were identical except for diffusion time, which was different for each experiment Since zinc dopes GaAs p-type, a p-n junction was created in each sample at the depth at which the zinc doping dropped below $N_D$. The junction depth was determined for each sample by metallurgical means and the depth was plotted against square root of time. In both investigations a straight-line graph was obtained and this was taken as proof of the $\sqrt{t}$ variation. However, it must be realised that this merely shows that the concentration $N_D$ progresses approximately as the square-root of time; in order for the Boltzman-Matano analysis to be valid the whole profile must progress in this way.

A number of experiments was therefore carried out in which radio-active zinc was diffused into GaAs from the vapour phase. The experimental details have been given in a previous publication [5]; the procedure may be summarised as follows. A slice of GaAs was encapsulated in an evacuated ampoule with small pieces of arsenic and radio-active zinc, and placed in a diffusion furnace set to 1000°C. All of the experiments used the same quantities of zinc and arsenic: the vapour pressures of zinc and arsenic in the ampoule were $1.7 \times 10^{-1}$ atm and $4 \times 10^{-2}$ atm respectively. These conditions were chosen to give profiles of the kind shown in fig. 2. Diffusion times were in the range 10 min to 30 h. After a slice had been diffused, layers were etched off, the amount of zinc in each layer counted and profiles were plotted. They are shown in fig. 4. The equilibrium surface concentration is $1.6 \times 10^{20}$ cm$^{-3}$ for all the profiles. In the figure the bulk part of the profile is extrapolated to the surface along a dotted line to give a pseudo-surface concentration, $C_0$. It may be seen that $C_0$ is different for each profile, progressing towards $c_S'$ with increasing time of diffusion. This variation in $C_0$ indicates a variation in profile shape with diffusion time, a point underlined in fig. 5 in which three of the profiles are plotted as functions of $x/\sqrt{t}$. According to the Boltzman-Matano assumptions these curves should be identical; this is clearly not so and it must be concluded that the assumptions are not justified in this case. In the next section reasons for this are suggested.

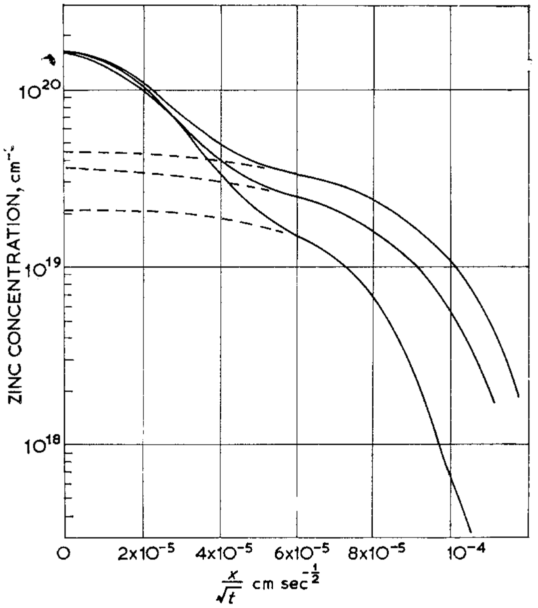

*Figure 5* Profiles A, D and E plotted using $x/\sqrt{t}$ as a parameter.

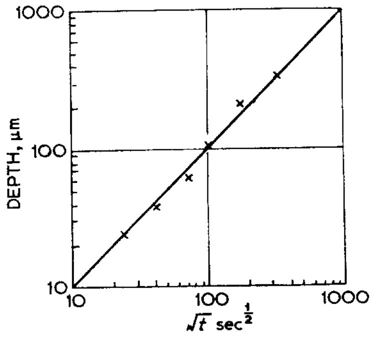

*Figure 6* Depth at which a profile falls to 1% of the surface concentration plotted as a function of $\sqrt{t}$.

It is worth comparing the data of fig. 4 with the work previously described in which junction depths were plotted as a function of $\sqrt{t}$. In fig. 6 is plotted the depth at which the profile drops to 1 % of the surface concentration, as a function of square root of diffusion time. A good straight line is obtained, agreeing with the previous work. The conclusion must be drawn that the junction-depth experiment is not adequate to test the Boltzman-Matano assumptions.

## 3. The Substitutional-Interstitial Mechanism

This mechanism was suggested by Frank and Turnbull [10] to account for the anomalous diffusion of copper in germanium. It has since been generalised by Sturge [11] and adapted by Chang and Pearson [12] to explain their results for zinc in GaAs. It is assumed that while the great majority of zinc atoms exist substitutionally on gallium sites in concentration $c_s$, a very small proportion, $c_i$, occur interstitially. The diffusion coefficient for the interstitials, $D_i$, is very much greater than that for substitutionals, $D_s$, and the interstitial atoms therefore dominate the diffusion process. The diffusion may be described as follows. The zinc atom joins the lattice at the surface, goes interstitial and diffuses through the lattice very fast. It eventually joins up with a gallium vacancy and becomes substitutional again. The crystal has now lost a vacancy, which it can replace either by one diffusing in from the surface or by some defect process occurring, such as dislocation climb. It is therefore possible for the number of vacancies to drop below the equilibrium number, if the crystal cannot replace vacancies as fast as they are being used up.

The two concentrations are related by an equation involving the gallium vacancies:

$$\mathrm{Zn_i}^+ + \mathrm{V} \rightleftharpoons \mathrm{Zn_s}^- + 2\mathrm{e}^+ \tag{5}$$

Here it is assumed that the interstitial zinc occurs as a singly ionised donor, as is suggested by recent isoconcentration work [4]. If it is assumed that there is instantaneous local equilibrium in the reaction of equation 5, then the law of mass action can be applied, giving

$$c_i = \frac{Kc_s(\gamma p)^2}{c_V} \tag{6}$$

where the substitutional concentration is virtually equal to the total concentration, $c_V$ is the gallium vacancy concentration and $\gamma$ is the activity coefficient for holes, approximately equal to unity under these conditions [4, 13]. For reasonably high concentrations, $c_s \simeq p$ and, denoting equilibrium values by primes, we have

$$K = \frac{c_i' \, c_V'}{c_s'^3} \tag{7}$$

Here $c_s'$ is the equilibrium solubility of substitutional zinc, which is effectively equal to the total solubility of zinc in GaAs under the conditions of the experiment. In a diffusion experiment, $c_S'$ should therefore correspond to the concentration of the profile when extrapolated back to the surface, i.e. $c_S' = 1.6 \times 10^{20}$ cm$^{-3}$ in the case of fig. 4.

If the diffusion coefficient of the substitutional zinc is considered negligible, the rate of increase of the zinc atoms may be written:

$$\frac{\partial c_i}{\partial t} + \frac{\partial c_S}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \tag{8}$$

and the corresponding equation for vacancies is:

$$\frac{\partial c_V}{\partial t} = D_V \frac{\partial^2 c_V}{\partial x^2} - \frac{\partial c_S}{\partial t} + k(c_V' - c_V) \tag{9}$$

where $D_V$ is the diffusion coefficient for vacancies. In equation 9, the first term on the right hand side represents vacancies gained by diffusion from the surface, the second represents loss of vacancies due to interstitial zinc going substitutional, and the third term is the bulk production of vacancies by dislocation climb, etc. At this stage the simplest possible assumption is made for this last term, namely that vacancies are produced at a rate proportional to the deviation of $c_V$ from its equilibrium value, with constant of proportionality, $k$. In general, the distribution with respect to time and distance would be found by solving these four equations.

Under the special circumstances of vacancy equilibrium being maintained, we have $c_V = c_V'$, the "$k$" term disappears and it is easily shown [5] that the equations reduce to

$$\frac{\partial c_S}{\partial t} = \frac{\partial}{\partial x}\left(D_0\, c_S^2 \frac{\partial c_S}{\partial x}\right) \tag{10}$$

where $D_0 = 3D_i\, c_i'/c_S'^3$. Equation 10 is of the form of equation 1, so under these circumstances it would be correct to analyse an experimental profile using the Boltzman-Matano analysis. If the "$k$" term cannot be ignored, the equations do not reduce to the form of Fick's law and the analysis would be inappropriate. In view of the experimental evidence outlined above, it would appear that this is sometimes the case. Equation 10 has in fact been solved numerically [14], so the solution may be treated as a known function. Let this solution be called

$$c_S = c_S'\, F(x, t) \tag{11}$$

where $F(x, t)$ varies in the range 0 to 1 and must be unity at $x = 0$ for all $t > 0$. From equation 6 and equation 7,

$$c_i = c_i'\, F^3 \tag{12}$$

Now consider the case of $k$ not negligible. If we can assume that under non-equilibrium conditions for vacancies diffusion of vacancies is small, then equation 9 becomes

$$\frac{\partial c_S}{\partial t} + \frac{\partial c_V}{\partial t} = k(c_V' - c_V) \tag{13}$$

Equation 11 will not hold for substitutional zinc in this case. Let us assume, however, that to a first approximation equation 12 is still a reasonable description of the interstitial distribution. This is essentially the same assumption as that made by Sturge [11]. It is justified physically on the grounds that a lack of vacancies will interrupt the flow of zinc atoms from the interstitial distribution to the substitutional distribution (as described by equation 5), but will not interfere very much with the original interstitial distribution providing the deviation from equilibrium is not very great. We then have:

$$c_V = \frac{c_V'}{(c_S'\, F)^3}\, c_S^3 \tag{14}$$

which, substituted in equation 13 gives

$$\frac{\partial c_S}{\partial t}\left\{1 + \frac{3c_V'\, c_S^2}{(c_S'\, F)^3}\right\} = kc_V'\left\{1 - \left(\frac{c_S}{c_S'\, F}\right)^3\right\} \tag{15}$$

We are interested in high zinc doping, and in this case $c_V'\, c_S^2 \ll (c_S'\, F)^3$ and the equation further simplifies to:

$$\frac{\partial c_S}{\partial t} = kc_V'\left\{1 - \left(\frac{c_S}{c_S'\, F}\right)^3\right\} \tag{16}$$

This amounts to saying that zinc atoms can join the lattice only at the rate at which the crystal can provide vacancies. The boundary condition for the equation is $c_S = 0$ for all $x$ at $t = 0$. Call the solution to this equation $c_S = f(x, t)$.

It is of interest to consider the circumstances under which the profile will be a solution either to equation 10 or to equation 16. The former implies no vacancy breakdown; $c_V = c_V'$. This condition would be expected to apply under conditions of low diffusion coefficients in which the take-up of vacancies occurs at a relatively low rate. Since $D$ is a very strong function of concentration, this would be under low-concentration conditions. There is, in fact, some evidence that the lower the values of $c$ (and $D$) being measured, the more satisfactory does the Boltzman-Matano analysis become [5]. The condition of vacancy equilibrium must also apply very close to a surface since a surface is effectively an infinite source of vacancies. In particular the surface concentration, at $x = 0$, should be the correct equilibrium concentration under all conditions. Thus equation 10 would be expected to be appropriate for the whole of any profile for which $c$ (and therefore $D$) are low. For profiles reaching high concentrations equation 10 must be correct at the surface and close to it and the profile must therefore commence with the form $c_s = c_s' F(x, t)$. In the bulk, however, equation 16 may be more appropriate and the profile may adopt the form $c_s = f(x, t)$. The profile measured in a radio-tracer experiment may therefore be a compromise between the former solution close to the surface and the latter solution in the bulk. It was shown in a previous note [6] that under these circumstances a diffusion profile similar to the experimental profiles of fig. 4 may be obtained. This is demonstrated in fig. 7. It remains to compute solutions of equation 16 and to compare them with the "bulk" profiles of fig. 4.

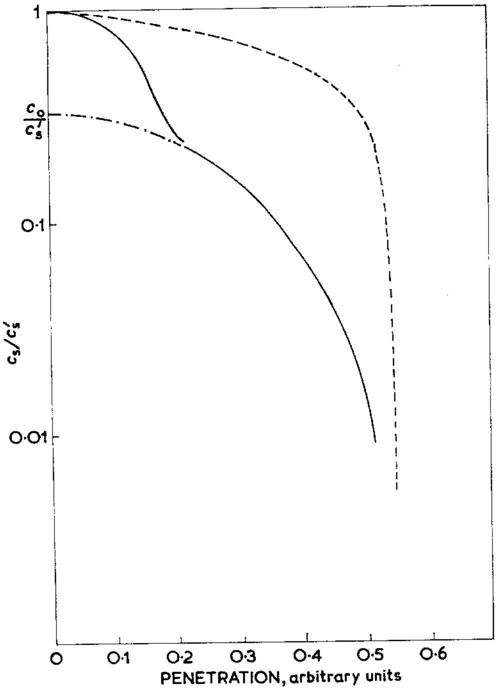

*Figure 7* Demonstrating how profiles of the type shown in fig. 4 might arise. The upper dotted curve is the "equilibrium profile" (solution to equation 10), the lower dotted curve is the solution to equation 16, which builds up to the equilibrium curve with increasing time. The full curve follows the former close to the surface and the latter in the bulk.

## 4. Computer Solutions

Solutions for equation 16 were computed using numerical values for the function $F(x, t)$ given in reference 14. The value of $D_0$ was taken from previous work [4] and $c_s'$ was taken as $1.6 \times 10^{20}$ cm$^{-3}$ to facilitate comparison with fig. 4. Four solutions are shown in fig. 8; these should be compared to experimental profiles A, B, C, D. Qualitatively the behaviour of the bulk profile agrees well with experiment, building up towards the equilibrium profile with increasing time, and the pseudo-surface concentration $c_0$ approaching $c_s'$. The shapes of the theoretical curves correspond quite well to the experimental ones and the penetration depths are similar. The values of $c_0$, however, do not agree well; the build-up towards $c_s'$ is faster in the case of the theoretical curves.

It seems possible that the discrepancy may be due to the simplification of assuming the quantity $k$ to be a constant. It is likely that bulk production of vacancies is due to climb of dislocations. $k$ will be related to the density of dislocations (which may itself be related to zinc

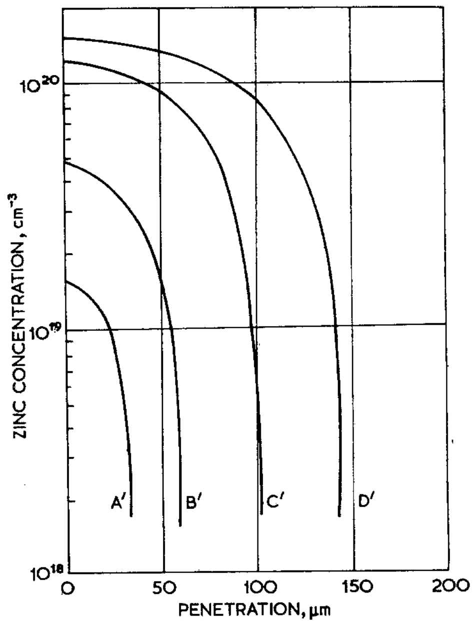

*Figure 8* Theoretical "bulk" profiles with $k$ as a constant for diffusion times of:

| | |
|---|---|
| Profile A' | 10 min |
| ,, B' | 30 min |
| ,, C' | 90 min |
| ,, D' | 3 h |

A value for $kc_v'$ of $2.6 \times 10^{13}$ cm$^{-3}$ sec$^{-1}$ was used in the calculations.

concentration) and to the rate at which they can climb, and might therefore be a complicated function of time and of the concentrations of zinc atoms and gallium vacancies. Clearly it would be possible to obtain a much better theoretical fit to the experimental curves by adopting some empirical relationship for $k$, since several fitting parameters would then be introduced. This is not considered worth doing at present, however, in view of the lack of experimental evidence on vacancy production.

## 5. Conclusions

An anomalous diffusion profile shape which occurs in a number of semiconductor systems has been considered for the case of zinc diffusion in GaAs. Radio-tracer profiles have demonstrated that the diffusion curves cannot be uniquely represented by taking $x/\surd t$ as a parameter and that the common device of analysing these profiles using the Boltzman-Matano graphical technique is therefore invalid. The theory of substitutional-interstitial diffusion has been discussed taking into account the possibility of the number of gallium vacancies dropping below the thermal equilibrium value, and theoretical profiles have been calculated which compare reasonably well with experiment. In obtaining this agreement, a value of one parameter had to be chosen, namely that for the quantity $kc_V'$. It should be noted, however, that the qualitative behaviour of the bulk profile obtained is independent of the value chosen for this quantity. The build-up of $f(x, t)$ towards $c_s' F(x, t)$ with increasing time and the approach of $c_0$ towards $c_s'$ are inherent in equation 16 and do not depend on the precise numbers put into the programme. Physically the parameter $k$ is probably related to the dislocation structure.

## Acknowledgement

We would like to thank Mr A. Baker of this department for permission to use fig. 1.

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