# Diffusion Properties of Cadmium in Indium Antimonide

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## ABSTRACT

Diffusion profiles of cadmium in indium antimonide were measured by a modified C-V technique and were found to exhibit anomalous behavior, as commonly found in III-V compounds. The general shape of the diffusion profile on a logarithmic scale is characterized by a concave region close to the surface followed by a steep front. The steep front is explained by the interstitial-substitutional diffusion mechanism. The concave region is theoretically shown to be related to a decrease of the diffusion coefficient near the surface. This decrease is assumed to be the result of the surface proximity rather than the result of a nonmonotonic concentration dependence of the diffusion coefficient. This surface effect is physically explained by an extension of the interstitial-substitutional model. Computer simulations based on this model give profiles similar to those experimentally measured.

Cadmium diffusion profiles in n-type indium antimonide exhibit a steep front near the p-n junction and a concave region (when plotted on a logarithmic scale) near the surface (1, 2). Such anomalous diffusion is commonly found in III-V compounds (3) and has been reported for zinc in GaAs (3, 4), InP (1), and InAs (1), phosphorus in GaAs (5), and other diffusion systems.

The basic interstitial-substitutional diffusion mechanism (6), which is usually invoked to interpret the steep front of the profiles, does not explain the concave region in the profiles, because it leads to profiles which are convex with a steep front. The concentration dependence of the diffusion coefficient, obtained from experimental profiles by applying the Boltzmann-Matano analysis (3), is nonmonotonic, exhibiting a maximum at intermediate diffusant concentrations (4, 5). Furthermore, the behavior near this maximum varies with diffusion time. This result, which is clearly unphysical, contradicts the monotonic dependence of the diffusion coefficient on the diffusant concentration as predicted by the interstitial-substitutional model. Consequently, the validity of the Boltzmann-Matano analysis for this type of diffusion has been doubted by some authors (4, 5), since the profiles cannot be expressed in terms of a single variable $x/\sqrt{t}$ (diffusion depth divided by the square root of diffusion time). The concave region in the profiles, which causes a peak in the results of a Boltzmann-Matano analysis, is assumed to be related to a surface effect on diffusion. A qualitative explanation of this phenomenon, relating it to a nonequilibrium of vacancies, has been given by Tuck (3).

The anomalous behavior described above was observed on a cadmium diffusion profile which was measured by means of a "graded C-V" technique described in the experimental section.

In the theoretical section, we present a generalization of the Boltzmann-Matano formula for the case of a diffusion coefficient dependent upon depth, diffusant concentration, and diffusion time. By means of this formula, phenomenological conclusions about the behavior of the diffusion coefficient are reached, showing that it decreases near the surface. Numerical results showing good qualitative agreement with experiment are presented, and suggestions are made about the physical reasons for the phenomenon.

## Graded C-V Profiling Method

The profile of electrically active cadmium diffused into the InSb was found from C-V measurements on MOS capacitors in several depths along the profile. This "graded C-V" technique is preferable to the well-

known radiotracer and resistivity methods because it eliminates the necessity for removal of successive thin layers. The method is based on gradual immersion of a long diffused sample in an etching solution so that the surface becomes a slightly slopy plane, along with which the impurity concentration is gradually changing. The surface type is changed from p to n where the wedge crosses the junction plane. A thin insulating layer is deposited on the sample, and a series of small electrodes are placed upon it to form MOS capacitors as shown schematically in Fig. 1.

From C-V measurements on a MOS capacitor at high frequency, the type of impurities in the crystal below it may be determined, and their concentration may be calculated from the ratio of minimum-to-maximum capacitance. Similar methods have been used for shallow implanted layers, but in those, the varying bias voltage controls the measurement depth, and the derivative $dC/dV$ of the measured curve is required to obtain the profile (7). In our experimental process, cadmium was diffused for several hours at 400°C into samples of tellurium-doped InSb with donor concentration of about $10^{15}$ cm$^{-3}$, cut along <111> plane and polished on the In face. After the diffusion, a slice about 2.5 cm long was gradually etched, so that a height difference of about 2 $\mu$m was obtained. A narrow strip along the sample had been protected by photoresist before the etching so that a step was formed, and the distance from every point on the wedged surface to the original surface could be determined by measuring the step height. A 1000Å pyrolitic SiO$_2$ layer was then deposited on the sample, and a series of 0.6 mm diam capacitors were formed on it by Cr-Au evaporation. C-V curves of these capacitors at 1 MHz were measured at 77°K.

The measured capacitance is equivalent to that of three capacitors in series: oxide capacitance $C_{ox}$, depletion capacitance $C_{dep}$, and the p-n junction capacitance $C_j$. The junction area is almost equal to the area of the whole sample, so that $C_j$ is large and thus may be neglected. One is left with the simple structure of a MOS capacitor at high frequency, and the ionized
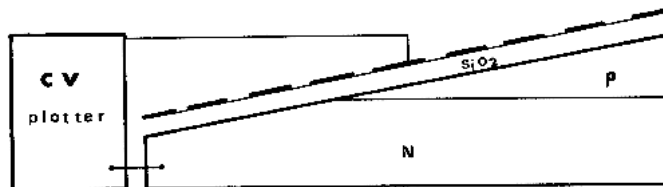


Fig. 1. Schematic setup for measurement of a diffusion profile by the graded C-V method. The impurity concentration below each MOS capacitor is found from the C-V curve.

impurity concentration $N_0$ may be readily obtained from the value of $C_{min}/C_{ox}$ which is a function of the oxide thickness and substrate doping level, by solving

$$\frac{N_0}{\phi_F} = \frac{4C_{ox}^2}{q\epsilon_{InSb}\epsilon_0 A^2} \left[ \frac{\dfrac{C_{min}}{C_{ox}}}{1 - \dfrac{C_{min}}{C_{ox}}} \right]^2 \qquad [1]$$

$C_{min}$ is the minimum of the $C-V$ curve, $\phi_F$ is the Fermi potential, $A$ is the capacitor area, and the other symbols have their usual meaning.

The accuracy of the graded $C-V$ method is determined by the following factors: (*i*) Variation of impurity concentration in the depletion region; (*ii*) variation of impurity concentration along the sloped surface under the metal electrode; (*iii*) minority-carrier generation by background illumination; (*iv*) magnification of capacitance-measurement error as $C_{min}/C_{ox} \rightarrow 1$ (see Eq. [1]; (*v*) inhomogeneity of the slope-etched surface; (*vi*) errors in the etching depth measurement.

For impurity densities above $5 \times 10^{16}$ cm$^{-3}$, the depletion layer width is less than 0.1 $\mu$m, so that the impurity concentration may be assumed to be constant throughout the depletion layer. Making a moderate slope on a long substrate eliminates the effect of concentration variation under the metal electrode. The effect of background illumination was found to be negligible from $C-V$ measurements on an n-type substrate with a known impurity concentration.

The minimum detectable change in capacitance is obtained for impurity concentrations below $10^{19}$ cm$^{-3}$. It may thus be concluded that the graded $C-V$ method is applicable for measurements of diffusion profiles in InSb for the range of impurity concentrations $5 \times 10^{16}$ cm$^{-3} \leq N \leq 10^{19}$ cm$^{-3}$.

Application of the graded $C-V$ method to our cadmium-diffusion process gave the profile shown in Fig. 2. The measured profile of active cadmium impurities is very similar to profiles measured by radiotracer methods. Hence, the results may be analyzed assuming that all the cadmium atoms are ionized. The surface concentration was too high to be measured by this technique, so the initial part of the profile may be extrapolated to the maximum solid solubility which is in the range of $4 \times 10^{19}$-$2.5 \times 10^{21}$ cm$^{-3}$ (8, 9). The spread of the measured values is believed to be mainly due to the nonuniformity of the etched surface, which was observed visually.

Inspection of the resulting profile motivated an investigation of the mathematical properties of the diffusion equation corresponding to such a diffusion profile. The treatment is given in the next section.

### Analysis of Diffusion Profiles

We assume that the diffusion process obeys Fick's law with an effective diffusion coefficient, $D$, which accounts for the detailed transport mechanism. For fixed temperature, surface concentration, and vapor pressures, $D$ may depend on the diffusant concentration $C$, the distance to the surface $x$, and the time $t$. The diffusion equation is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D(C, x, t)\, \frac{\partial C}{\partial x} \right] \qquad [2]$$

The initial conditions are $C(x) = 0$ for $x > 0$, and the boundary conditions (constant source diffusion) are

$$\left. \begin{array}{l} C(o, t) = C_o \\[1em] C(\infty, t) = 0 \end{array} \right\} \qquad [3]$$

It is usually assumed in the literature that $D$ is a function of $C$ only.

These are the conditions for application of the standard Boltzmann-Matano analysis, which gives the
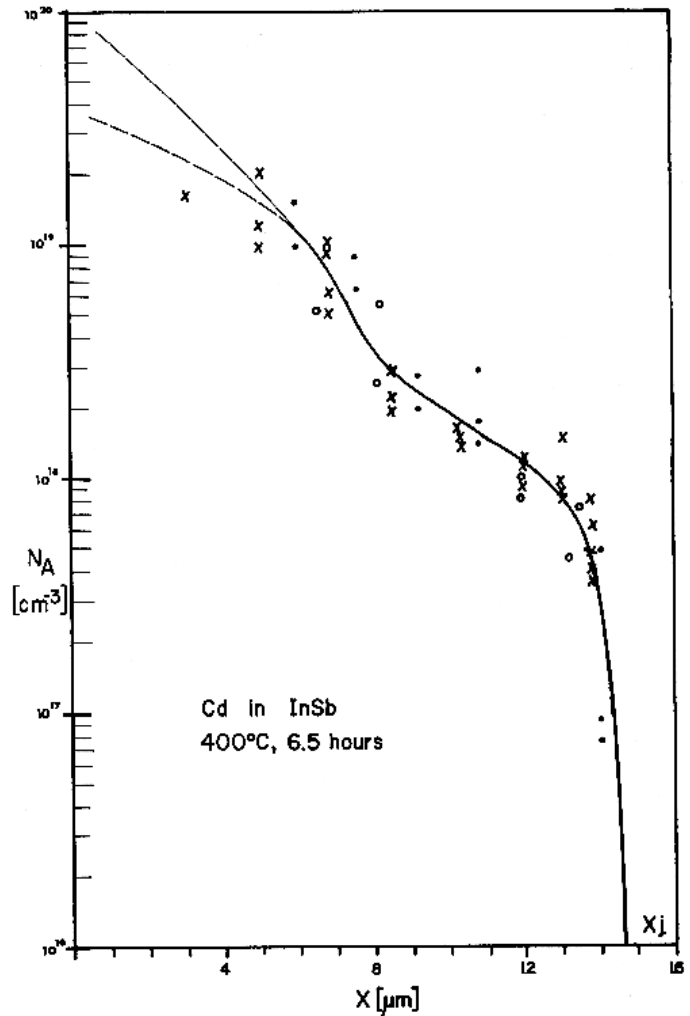


Fig. 2. Diffusion profile of Cd in InSb, measured by the graded $C-V$ method. Experimental points represent several capacitors on three samples. The surface concentration was too high to be measured by this technique.

value $D(C_1)$ at any concentration $C_1$ on an experimentally-measured profile $C(x)$ as (5)

$$D(C_1) = -\frac{1}{2t_1}\left(\frac{dx}{dC}\right)_{C_1} \int_o^{C_1} x\, dC \qquad [4]$$

where $t_1$ is the diffusion time used in the experiment.

Functions $D(C)$ that were obtained by applying Eq. [10] on profiles measured by us and by others (1, 9), are given in Fig. 3. Functions of similar behavior were calculated in GaAs for Zn (4) and P (5). The increase in $D(C)$ with increasing $C$ at the low concentrations range is a consequence of the steepness of the experimental profile at the diffusion front and is physically explainable by the interstitial-substitutional diffusion mechanism (7).

The peak in $D(C)$ at intermediate concentrations reflects the existence of a concave region in the profiles. The fact that the peak of $D(C)$ is time-dependent (4) leads to the conclusion that the validity of the results is in doubt. The peak in $D(C)$ is physically unfeasible: it is the outcome of applying Eq. [4] near the surface, and probably is not representative of bulk diffusion (5). In fact, the diffusion depth of such profiles, plotted *vs.* square root of diffusion time, is not a straight line through the origin (4), indicating that a diffusion coefficient which depends only on the diffusant concentration as in Eq. [2] does not represent the actual diffusion process. It is reasonable to assume that in the actual process there is a dependence of $D$ on $x$ which is responsible for special behavior near the surface, and our previous assumption that a concentration dependence may account for it led us to an unphysical result.

In a more general case, $D(C)$ in Eq. [2] may be replaced by a function $D(x, C, t)$, dependent on depth, diffusant concentration, and diffusion time.

Following the steps for derivation of the Boltzmann-Matano formula (3) without any restricting conditions on $D$, we obtain

$$D(x_1, \hat{C}_1, t_1) = -\frac{1}{2t_1} \frac{\int_0^{\hat{C}_1} x \, dC}{\left.\frac{\partial \hat{C}}{\partial x}\right|_{C=\hat{C}_1}} \qquad [5]$$

where $\hat{C}(x, t_1)$ is a known profile at a certain time $t_1$.

This is a generalization of the Boltzmann-Matano formula, giving the local value of $D$ in a single point of a three-dimensional space. If $D$ depends only on $C$, all the information about $D(C)$ may be extracted from a single experimental profile by means of Eq. [5], but an infinite number of profiles is required for doing so in the general case. Hence, Eq. [5] is not very useful without further assumptions.

With the aid of Eq. [5] we can now prove that a concave region of the diffusion profiles on a logarithmic scale indicates that $D$ is increasing in that region from the surface toward the bulk.

The fact that the profile is concave may be expressed by (see Fig. 4)

$$-\frac{\partial}{\partial x}(\ln C)\big|_{x_1} > -\frac{\partial}{\partial x}(\ln C)\big|_{x_2} \qquad [6]$$

where $(x_1, C_1)$ and $(x_2, C_2)$ are two points on the profile, and $x_1 < x_2$.

By Eq. [5], the ratio of the values of $D$ in these points is

$$\frac{D_1}{D_2} = \frac{\left.\frac{\partial C}{\partial x}\right|_{x_2}}{\left.\frac{\partial C}{\partial x}\right|_{x_1}} \cdot \frac{\int_0^{C_1} x \, dC}{\int_0^{C_2} x \, dC}$$

$$= \frac{\left.\frac{\partial C}{\partial x}\right|_{x_2}}{\left.\frac{\partial C}{\partial x}\right|_{x_1}} \left[1 + \frac{\int_{C_2}^{C_1} x \, dC}{\int_0^{C_2} x \, dC}\right]$$

$$< \frac{\left.\frac{\partial C}{\partial x}\right|_{x_2}}{\left.\frac{\partial C}{\partial x}\right|_{x_1}} \left[1 + \frac{(C_1 - C_2)x_2}{C_2 x_2}\right]$$

$$= \frac{\left.\frac{\partial C}{\partial x}\right|_{x_2}}{\left.\frac{\partial C}{\partial x}\right|_{x_1}} \cdot \frac{C_1}{C_2} = \frac{\frac{\partial}{\partial x}(\ln C)\big|_{x_2}}{\frac{\partial}{\partial x}(\ln C)\big|_{x_1}} \qquad [7]$$

From inequality [6] it follows that

$$\frac{\frac{\partial}{\partial x}(\ln C)\big|_{x_2}}{\frac{\partial}{\partial x}(\ln C)\big|_{x_1}} < 1 \qquad [8]$$

and by substituting Eq. [8] in Eq. [7] we have

$$\frac{D_1}{D_2} < 1 \qquad [9]$$

### Discussion

By inspection of diffusion profiles having a concave region near the surface and a steep front, in light of
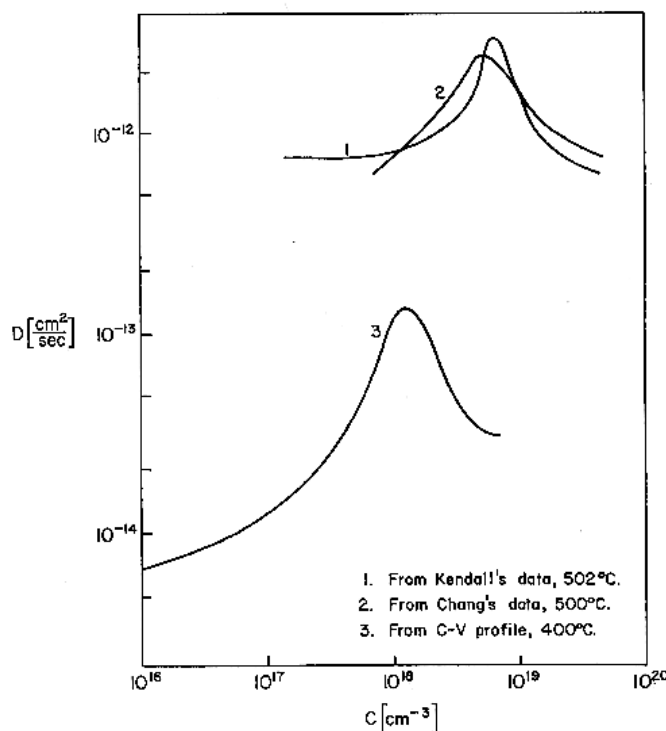


Fig. 3. Concentration dependence of the diffusion coefficient resulting from Boltzmann-Matano analysis of experimentally measured Cd profiles in InSb.
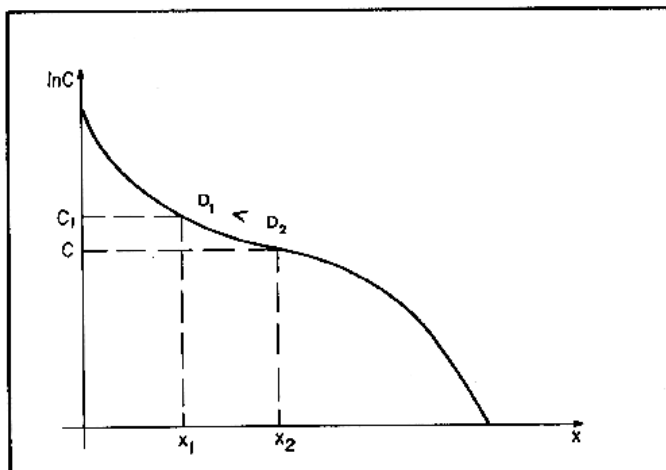


Fig. 4. Two points in the concave region of a diffusion profile. The diffusion coefficient increases with increasing depth in this region.

the previous section it may be concluded that: (*i*) Deep in the bulk (where the cadmium concentration is low), the local diffusion coefficient is decreasing along the $x$ direction, causing a profile with a steep front; (*ii*) Near the surface, the local diffusion coefficient is increasing along the $x$ direction, causing a concave region in the profile.

It is physically reasonable to relate the first phenomenon to a concentration dependence of $D$ (6), and the second to the variable $x$ (*i.e.*, to an effect of the surface proximity on $D$). Ignoring any possible variations of the model in time, the behavior of $D$ may be explained qualitatively by a family of curves as shown in Fig. 5, describing a function $D(x, C)$ that increases with $C$ and increases with $x$ for small values of $x$. If we mark a decreasing series of concentrations (representing a diffusion profile) on the curves, we get a distribution $D(x)$ with a maximum somewhere below the surface. A plot of this distribution *vs.* $C$ will exhibit the same properties as the curves in Fig. 3. This explains the existence of a maximum in the $D(C)$
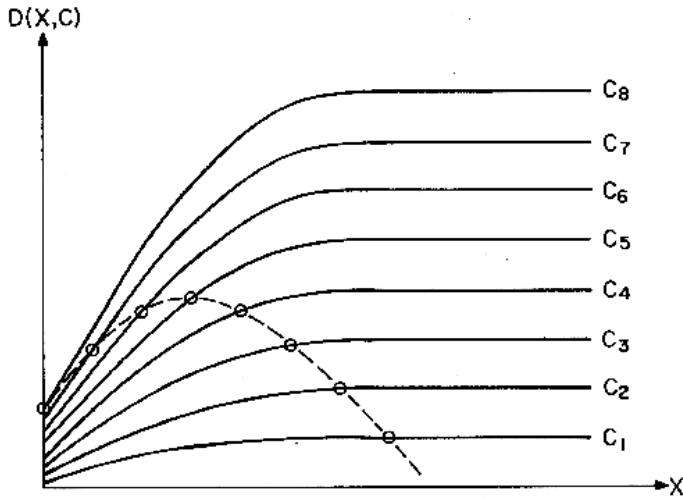
Fig. 5. Curves representing a diffusion coefficient $D(x, C)$ which increases with $C$ and increases with $x$ near the surface. By plotting $D(x)$ along a diffusion profile a peak is obtained.



Fig. 6. Diffusion profiles calculated by the computer using the $D(x, C)$ model, for $t = 3, 6, 9, \ldots$ hr.

curve calculated by the standard Boltzmann-Matano method.

The concentration dependence of $D$ is usually explained by the interstitial-substitutional diffusion mechanism with charged interstitial species (6, 3). Another mechanism, based on charged vacancies, has also been proposed for diffusion of Cd in InSb (9). The dependence on $x$ may be explained by an extention of the interstitial-substitutional model.

Following the derivation of the standard interstitial substitutional model (3, 6), it may be shown that

$$D(C) = K \frac{D_i}{C_v} C^n \qquad [10]$$

where $D_i$ is the interstitial diffusion coefficient, $C_v$ is the vacancy concentration, $n$ depends on the interstitial charge, and $K$ is a constant. In the derivation of Eq. [10], $C_v$ was assumed to be constant throughout the sample. Now, if we assume that the surface supplies vacancies to the bulk during the diffusion process, so that the vacancy concentration $C_v$ is decreasing from the surface towards the bulk, $D$ might be expressed in an extended form of Eq. [10]

$$D(x, C, t) = KD_i \frac{C^n}{C_v(x, t)} \qquad [11]$$

In Eq. [11], $C_v(x, t)$ is the vacancy profile which diffuses simultaneously with the cadmium. Each of the curves depicted in Fig. 5 is proportional to the reciprocal of the vacancy profile. Our assumption about the vacancies implies that the interstitial-to-substitutional ratio increases along the $x$ direction near the surface, causing a corresponding increase in diffusion coefficient. Since the incoming vacancies are consumed by interstitials going substitutional, it is reasonable to make a first-order assumption that a stationary vacancy profile is established, thus obtaining a model which does not depend on time. Numerical experiments with the model also support this assumption.

A computer routine for solving a general quasilinear parabolic partial differential equation, of which Eq. [2] is a special case, has been written, such that all the coefficients are parameters and may depend on $x$, $C$, and $t$. The program is based on a stable three-time-level method described by Mitchell (10), and uses Richardson's extrapolation for automatic stepsize control. Computational experiments with that program actually served as motivation for a part of the theory described above. Figure 6 shows theoretical profiles obtained for a diffusion coefficient of the form (10) where $n$ was chosen to equal 1, and $C_v(x, t)$ was arbitrarily assumed to be of the form $1 + K_1 \cdot \exp(-x/L)$, where $L$ is a "vacancy diffusion length" and $K_1$ is a constant. A qualitative agreement with experi-
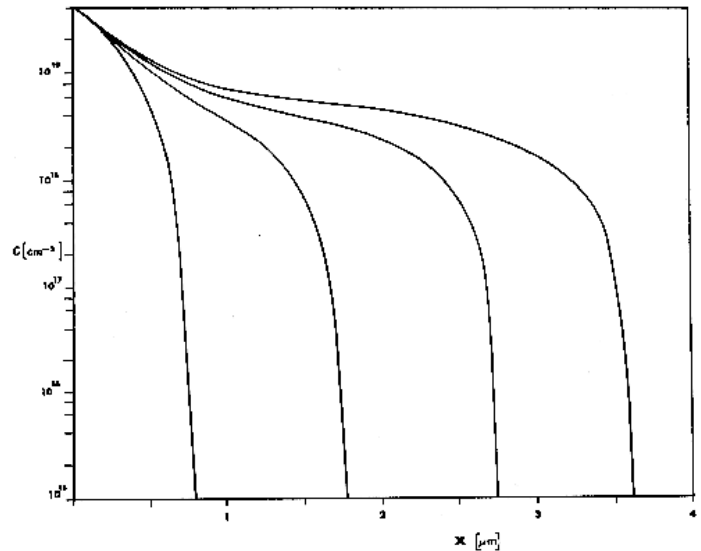
ment was clearly obtained: the profiles have a steep front (caused by $C^n$) and a concave section appears after a certain diffusion time. An exact quantitative agreement with experiment in InSb could not be obtained, due to lack of data, so that $n$ could not be picked optimally, and it was impossible to fit the function $C_v$ exactly.

Figure 7 shows diffusion depth $vs.$ $\sqrt{t}$, as obtained from the computer results. The junction depth is observed to grow slowly in the initial stage, then continues in a straight line that does not cross the origin.
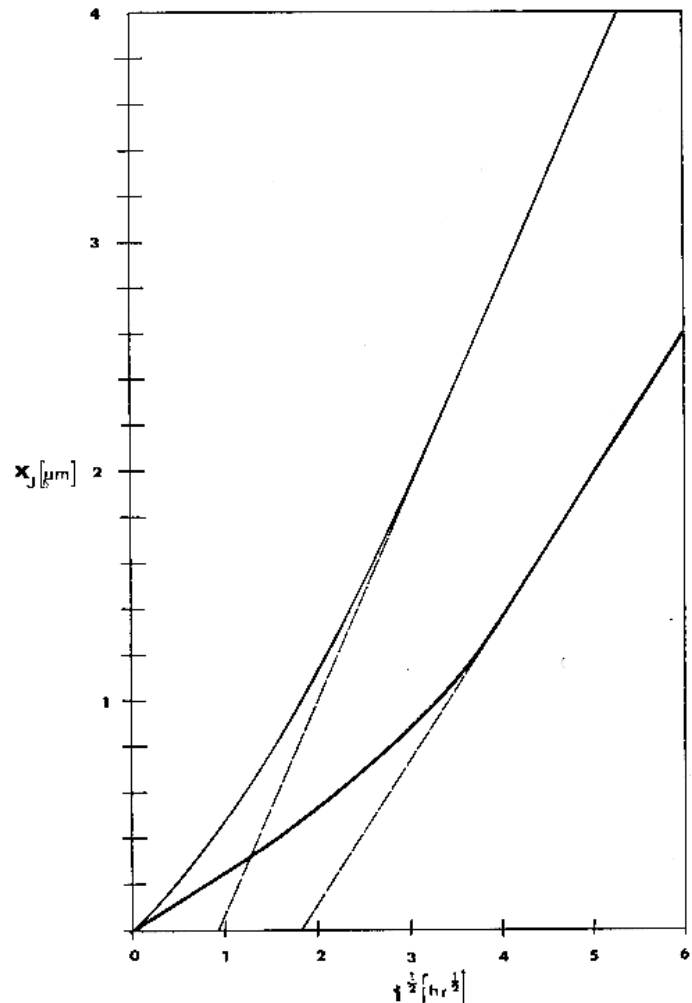


Fig. 7. Diffusion depth vs. square root of diffusion time, calculated using the $D(x, C)$ model for two different parameter sets.

Experimental results of exactly the same nature were published by Ting and Pearson (4) for zinc in GaAs.

## Conclusions

A generalization of the Boltzmann-Matano analysis for diffusion profiles has been presented. As a corollary, it has been shown that a concave region in constant-source diffusion profiles (on a semilogarithmic scale) indicates that the diffusion coefficient is increasing in that region toward the bulk. By analysis and synthesis of constant-source diffusion profiles, it has been shown that the outstanding properties of diffusion of various impurities in III-V compounds may be characterized by a nonlinear diffusion coefficient which depends both on the diffusant concentration and the distance from the surface. Time dependence of the diffusion coefficient seems to be negligible. Such a diffusion coefficient may represent an interstitial-substitutional diffusion mechanism with a surface-effect that reduces the diffusion constant at small depths. An extension of the interstitial-substitutional model, assuming an enhanced vacancy concentration near the surface, has been suggested to explain this effect. The model has been implemented on a computer, and theoretical profiles that have been produced show a good qualitative agreement to experiment in shape and time dependence of the diffusion depth.

## Acknowledgments

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