that in discussing F_{var} it has been assumed that the $\psi_\mu{}^i$ and $\Psi_{\{\mu\}}$ form complete orthonormal sets, whereas in the case of F_a it is desired to permit the sets $\{\psi_\mu{}^i\}$ to be incomplete. Such an incomplete set can be constructed by omitting from a complete set certain functions $\psi_\rho{}^i$. Now let F_{var} be computed using for the P's nonoptimal values: zero for the P's corresponding to the omitted ψ's, and for the other P's solutions of Eq. (2.10) as constructed with the incomplete set of ψ's. Use of these nonoptimal values yields $(F_a)_P$, but certainly increases the value of F_{var}. Finally, use of nonoptimal values of the P's in computing F_a yields

$$F_a \geqslant (F_a)_P \geqslant (F_{\text{var}})_P \geqslant F.$$

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Dependence of the Diffusion Coefficient on the Fermi Level: Zinc in Gallium Arsenide

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The experimental variation of the diffusion coefficient D with Zn concentration C_s has been determined at 1000, 900, 800, and 700°C from radioactive ^{65}Zn diffusion profiles by a Boltzmann-Matano analysis. With interstitial Zn as the dominant diffusing species and its concentration controlled by the interstitial-substitutional equilibrium in which the singly ionized interstitial donor reacts with a neutral Ga vacancy to form a singly ionized substitutional acceptor and two holes, the effective diffusion coefficient is described by $D=D^*C_s^2\gamma_p^2[1+(C_s/2\gamma_p)(d\gamma_p/dC_s)]$, where γ_p is the hole activity coefficient. The term D^* equals $2D_i/K_1 p_{As_4}{}^{1/4}$, where D_i is the interstitial diffusion coefficient, K_1 the reaction equilibrium constant, and p_{As_4} the As_4 pressure. The relationship between γ_p and the Fermi level E_f is given by $\gamma_p=(A/p)\exp(E_f/kT)$, where A is a constant dependent only on temperature and p is the hole concentration. This derivation for D has extended previous analyses to include both the built-in field and the nonideal behavior of holes which occurs when the impurity level broadens into an impurity band and merges with the valence band to form impurity-band tails at high Zn concentrations. The observed nonmonotonic dependence of the Zn diffusion coefficient on its concentration is a consequence of the nonideal behavior of holes at high concentrations. Quantitative comparison of D with the experimental concentration dependence has permitted the determination of γ_p and E_f as functions of the hole concentration.

I. INTRODUCTION

FROM the study of Zn diffusion in GaAs by Cunnell and Gooch,[1] the noncomplementary error function shape of the Zn-concentration–versus–distance curves was clearly demonstrated. The resulting diffusion coefficients as a function of Zn concentration revealed a concentration-dependent diffusion coefficient (see Ref. 2 and Sec. III B for a description of the determination of the diffusion coefficient D from the diffusion profile by the Boltzmann-Matano method). Longini[3] contributed significantly to the understanding of the diffusion mechanism by suggesting an interstitial-substitutional model in which the more rapidly diffusing interstitial donor dominates the diffusion process at high-substitutional concentrations. Weisberg and Blanc[4] considered the interstitial-substitutional diffusion suggested by Longini for a fully ionized substitutional acceptor and the interstitial species as either (a) neutral, (b) a single donor, or (c) a double donor. They found that the singly ionized interstitial donor gave the best fit to the 1000°C diffusion profiles of Cunnell and Gooch, which meant that the diffusion coefficient varied as the square of the substitutional Zn concentration.

It should be noted that in their diffusion experiments Cunnell and Gooch used a two-zone heating system to reduce the vapor pressure of the Zn (which also reduces the partial pressure of arsenic vapor species), and obtained diffusion profiles only for surface concentrations between 2 and 8×10^{19} cm^{-3} which is considerably lower than the pseudobinary solubility of 3.5–4.0×10^{20} cm^{-3}.[5,6] Data over a more extensive range of concentrations were provided by the diffusion studies of Kendall

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[2] P. G. Shewmon, *Diffusion in Solids* (McGraw-Hill Book Company, Inc., New York, 1963), p. 28.
[3] R. L. Longini, Solid State Electron. **5**, 127 (1962).
[4] L. R. Weisberg and J. Blanc, Phys. Rev. **131**, 1548 (1963).
[5] L. L. Chang and G. L. Pearson, J. Phys. Chem. Solids **25**, 23 (1964).
[6] M. B. Panish and H. C. Casey, Jr., J. Phys. Chem. Solids **28**, 1673 (1967).

and Jones,[7] who obtained profiles with surface concentrations at or near the pseudobinary solubility. By use of the isoconcentration-diffusion technique,[7] Chang and Pearson[8] were able to obtain directly the diffusion-coefficient values as a function of concentration. To obtain a suitable fit over the more extensive concentration range, they found it necessary to consider the interstitial species as a doubly ionized donor, the substitutional Zn as both ionized and neutral, and an activity coefficient for holes.

Within the framework of the theories accepted at that time, the assumptions by Chang and Pearson were reasonable. At concentrations in excess of one-tenth the effective density of states, the activity coefficient of holes γ_p had been predicted to become greater than unity.[9] The lower concentrations considered by Weisberg and Blanc did not employ or require activity-coefficient considerations. Several recent studies have provided additional insight into the treatment of impurities at very high concentrations. Experimentally a one-to-one correspondence between free holes and Zn atoms has been found,[6,10,11] and at any temperature un-ionized Zn occurs only for concentrations less than 5×10^{18} cm^{-3}.[10] Therefore, the substitutional Zn must be taken as fully ionized at high concentrations. The accepted theory for the activity coefficients for electrons and holes did not consider the impurity level broadening into an impurity band and merging with the valence band to form impurity-band tails at very high concentrations. The results of Halperin and Lax[12] permit a numerical evaluation of this effect, and γ_p was found to be less than 1 rather than greater than 1 as previously predicted (see Ref. 6 for a complete discussion). Recently, the consideration of Zn as fully ionized at high concentrations and a concentration-dependent density of states was necessary in order to reconcile the 1000°C experimental solid solubility for Zn in GaAs.[6] The purpose of this paper is to extend the concepts utilized in the solubility treatment[6] to the analysis of the experimental diffusion profiles.

The effective diffusion coefficient has been obtained with a mathematical treatment similar to that used by Chang and Pearson[8] with the Zn and vacancy charge states given by Weisberg and Blanc,[4] but with the inclusion of the built-in field and the nonideal behavior of holes as represented by a concentration-dependent γ_p. The inclusion of γ_p in the diffusion analysis permits understanding the nonmonotonic variation of the experimental D with C_s. Theoretical arguments have

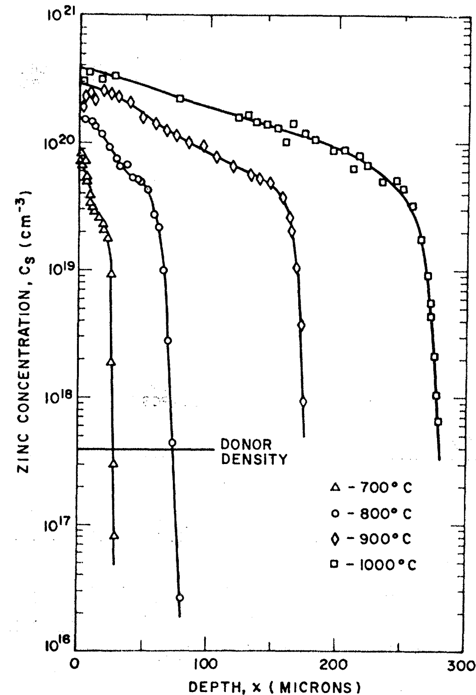

FIG. 1. Diffusion profiles of Zn in GaAs at 700, 800, 900, and 1000°C. Diffusion time is normalized to 1.5 h.

shown that γ_p is unity at low concentrations and less than unity at very high concentrations, but at the present time no calculated values of γ_p can be obtained in the concentration range between these limiting cases. By comparison of the calculated and experimental D, and with the assumption that the variation of D from a concentration-squared behavior is due entirely to changes in γ_p, the quantitative behavior of γ_p and the Fermi level E_f may be obtained in the concentration range between the localized level and impurity-band tailing. Thus, the diffusion analysis not only provides further insight into the mechanism of diffusion, but also provides quantitative information on the behavior of semiconductors at high concentrations.

II. EXPERIMENTAL DIFFUSION PROFILES

Diffusion profiles were obtained by diffusing radioactive ^{65}Zn from a source of the order of milligrams into 25-mil-thick GaAs wafers in a fused silica ampoule with a volume of about 2 cm^3. The source and wafers were maintained at the same temperature. The diffusion profiles are shown in Fig. 1 where the diffusion time was 1.5 h for the 800, 900, and 1000°C profiles and 168 h for the 700°C profile. The 700°C profile has been normalized to 1.5 h according to the relation $C_s=C_s(x/t^{1/2})$. The diffusion profiles were determined in terms of the Zn concentration C_s versus depth x by comparing the 1.12-MeV γ activity of each section removed by lapping with that of a calibrated ^{65}Zn standard. The method

[7] D. L. Kendall and M. E. Jones, in American Institute of Electrical Engineers–Institute of Radio Engineers Device Research Conference, Stanford University, 1961 (unpublished).
[8] L. L. Chang and G. L. Pearson, J. Appl. Phys. **35**, 1960 (1964).
[9] A. J. Rosenberg, J. Chem. Phys. **33**, 665 (1960).
[10] F. Ermanis and K. Wolfstirn, J. Appl. Phys. **37**, 1963 (1966).
[11] M. G. Mil'vidskii and O. V. Pelevin, Izv. Akad. Nauk SSSR, Neorgan. Materialy **1**, 1454 (1965) [English transl.: Bull. Acad. Sci. USSR, Inorg. Mater. **1**, 1328 (1965)].
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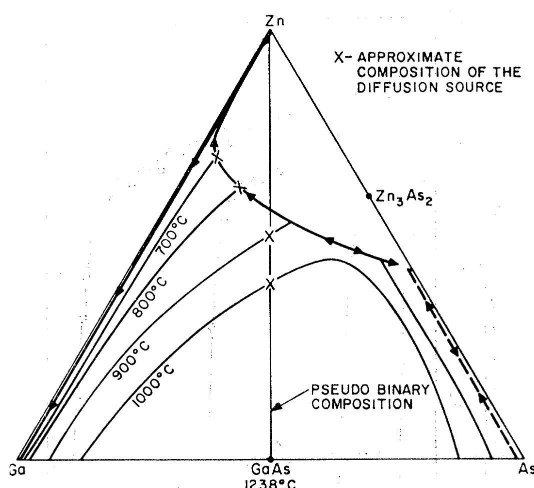

FIG. 2. The Ga-As-Zn ternary-phase diagram illustrating the approximate compositions of the diffusion sources.

is described in more detail in Ref. 13. One isoconcentration point was determined at 1000°C in a manner identical to that reported in Ref. 8.

It should be noted that when an elemental-Zn source is used in the manner described here, there is an initial small amount of damage to the surface of the sample as a ternary liquidus is established. The ternary-liquidus composition is not necessarily on the pseudo-binary, since a small amount of Zn and As are in the vapor phase. At temperatures below about 855°C the liquidus composition is greatly affected by the presence of the Zn_3As_2 phase.[14] The approximate final-liquidus compositions for the diffusion sources used in this work are shown in the ternary-phase diagram[14] of Fig. 2. It has been assumed that the amounts of Zn and As in the vapor are small compared with the amount of elemental Zn placed in the ampoule.

The concentration-dependent diffusion coefficient has been obtained from the profiles by the Boltzmann-Matano method (Sec. III B) and serves as the experimental data for obtaining the relation of the Fermi level to the diffusion coefficient. For the analysis presented in the following section, the precise composition of the diffusion source is not important. It should be noted, however, that for comparison of this diffusion data with other diffusion studies, it is necessary to know precisely the composition of the diffusion sources.

III. ANALYSIS

A. The Effective Diffusion Coefficient and Interstitial-Substitutional Equilibrium

In this analysis of diffusion, both the equilibrium between the interstitial and substitutional Zn and the effects of the built-in field[15] are included in the expressions for the total flux of Zn atoms. The total flux J_{Zn} is the sum of the interstitial and substitutional flux, each of which consists of a flux term due to the concentration gradient and a flux term for the built-in field. Also, the experimental conditions permit the analysis as a one-dimensional problem. The resulting one-dimensional expression for the total flux along x is

$$J_{\mathrm{Zn}}=-D_i(\partial C_i/\partial x)\pm\mu_iC_i\mathcal{E}-D_s(\partial C_s/\partial x)\pm\mu_sC_s\mathcal{E}, \quad (1)$$

where D_i is the diffusion coefficient of the interstitial species and C_i its concentration, D_s and C_s the substitutional diffusion coefficient and concentration, and $\mathcal{E}$ the built-in field. The proper sign for the field term is determined by both the sign of the field and the sign of the ionized carrier. The mobility μ is related to the diffusion coefficient by the expression referred to as the Einstein equation

$$\mu=qD/kT, \quad (2)$$

where q is the electronic charge, and kT the Boltzmann-constant–absolute-temperature product.

For conditions of equilibrium between the holes and electrons there can be no net flow of electric current, so that in inhomogeneous material a built-in field must exist to counteract the current due to diffusion by the potential gradient. The most mobile of the species present in the largest concentration will dominate the expression for current, i.e., the hole current i_p

$$i_p=-q\mu_p p[(1/q)\partial(E_f-E_0)/\partial x-\mathcal{E}]=0, \quad (3)$$

where μ_p is the hole mobility and p the hole concentration. The difference between E_f, which is the chemical potential of holes, and the reference potential energy E_0 is given by[6,16]

$$E_f-E_0=kT\ln\gamma_p p+\text{constant}, \quad (4)$$

where the constant term includes the use of p in number/cm^3 rather than atom fraction and the choice of the position of E_0. The reference potential E_0 is usually taken as one of the band edges or the location of the Fermi level in intrinsic material. Equation (4) represents the thermodynamic relationship of chemical potential to concentration as required by the first and second laws of thermodynamics.[16] The activity coefficient of holes, as defined here by Eq. (4), is utilized because the diffusion expressions are simpler mathematically with γ_p than with E_f. Therefore, the built-in field is

$$\mathcal{E}=\frac{1}{q}\frac{\partial(E_f-E_0)}{\partial x}=\frac{kT}{q}\left(\frac{1}{p}\frac{\partial p}{\partial x}+\frac{1}{\gamma_p}\frac{\partial\gamma_p}{\partial x}\right). \quad (5)$$

For a constant γ_p, Eq. (3) may be written in terms of the usual diffusion coefficient times the hole gradient. Whenever a species in a current (flux) equation departs from ideality, as shown by a nonconstant activity coefficient, the diffusion term normally written as a

[13] L. L. Chang and G. L. Pearson, J. Appl. Phys. **35**, 374 (1964).
[14] M. B. Panish, J. Electrochem. Soc. **113**, 861 (1966).
[15] P. G. Shewmon, *Diffusion in Solids* (McGraw-Hill Book Company, Inc., New York, 1963), pp. 23, 122, and 140.
[16] R. A. Swalin, *Thermodynamics of Solids* (John Wiley & Sons, Inc., New York, 1962), p. 253.

FIG. 3. Diffusion coefficient of Zn in GaAs versus Zn concentration at 1000°C as derived from a Boltzmann-Matano analysis.

concentration gradient times a diffusion coefficient must be written as a potential gradient times a mobility-concentration product[15] as in Eq. (3). Equation (5) may be used for the field term in the total flux of Eq. (1). Then substitution of J_{Zn} into the continuity equation gives

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left[D_i\frac{\partial C_i}{\partial C}\mp\mu_iC_i\left(\frac{kT}{p}\frac{\partial p}{\partial C}+\frac{kT}{\gamma_p}\frac{\partial\gamma_p}{\partial C}\right)+D_s\frac{\partial C_s}{\partial C}\mp\mu_sC_s\left(\frac{kT}{p}\frac{\partial p}{\partial C}+\frac{kT}{\gamma_p}\frac{\partial\gamma_p}{\partial C}\right)\right]\frac{\partial C}{\partial x},\qquad(6)$$

where the total Zn concentration $C=C_i+C_s$, and $(\partial/\partial x)$ has been replaced by $(\partial/\partial C)(\partial C/\partial x)$. From Eq. (6) an effective diffusion coefficient $D=-J_{Zn}/(\partial C/\partial x)$ may be identified as

$$D=D_i\frac{\partial C_i}{\partial C}\mp D_iC_i\left(\frac{1}{p}\frac{\partial p}{\partial C}+\frac{1}{\gamma_p}\frac{\partial\gamma_p}{\partial C}\right)+D_s\frac{\partial C_s}{\partial C}\mp D_sC_s\left(\frac{1}{p}\frac{\partial p}{\partial C}+\frac{1}{\gamma_p}\frac{\partial\gamma_p}{\partial C}\right).\qquad(7)$$

The proper designation of the sign for the interstitial and substitutional field terms depends on the charge state of the interstitial and substitutional species. Ions of charge state identical to that of the dominant free carrier (the hole) will be retarded and have a minus sign in Eq. (7), while oppositely charged ions will be aided and enter Eq. (7) as the plus sign.

At equilibrium the interstitial Zn, all of which is assumed to be singly ionized, reacts with a neutral Ga vacancy to form an ionized substitutional Zn acceptor and two holes:

$$Zn_i^+ + V_{Ga}\rightleftarrows Zn_{Ga}^- + 2e^+.\qquad(8)$$

For these charge states, the built-in field will retard C_i and aid C_s. Since the equilibrium Ga vacancy concentration in the solid is proportional to the fourth root of the As_4 pressure, the equilibrium reaction gives C_i as

$$C_i=C_s(\gamma_p p)^2/K_1 p_{As_4}^{1/4},\qquad(9)$$

with the activity coefficient of substitutional Zn taken as constant. At the concentrations considered here ($C_s>10^{18}$ cm^{-3}), the hole concentration equals C_s[6,10,11]

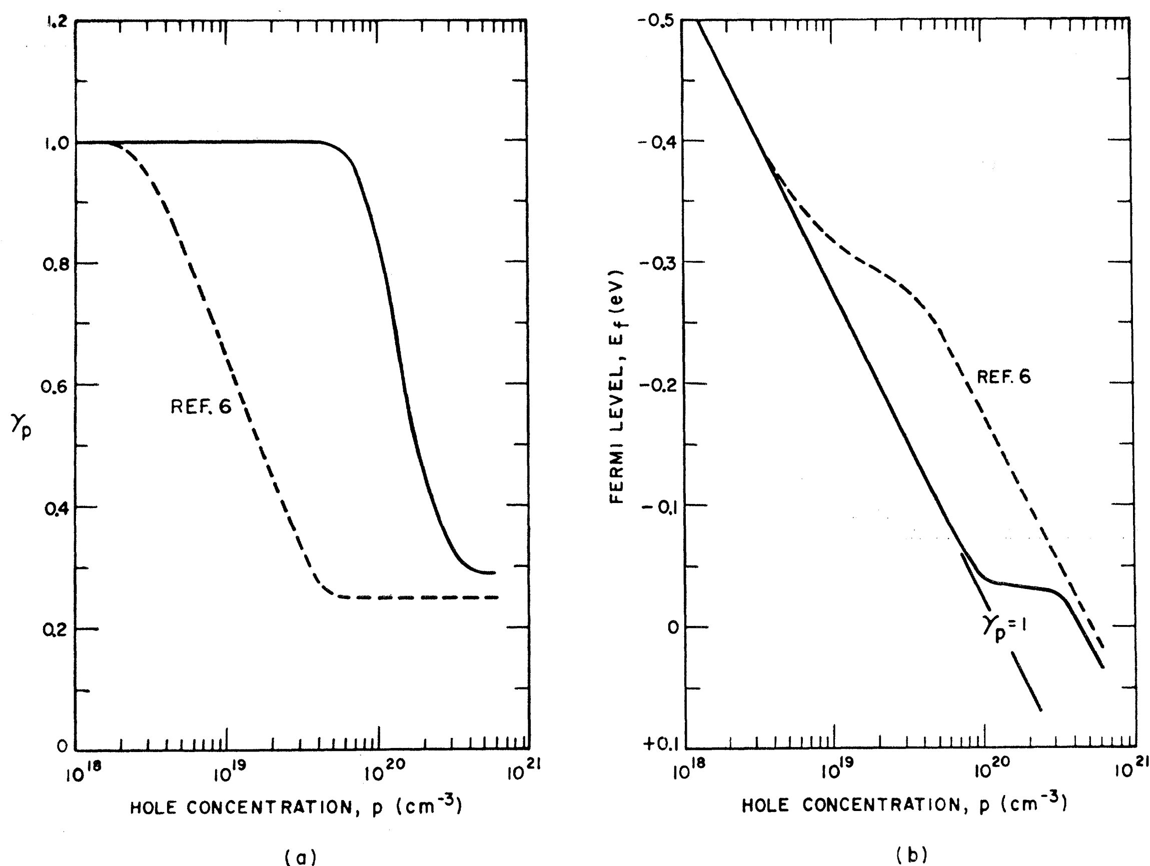

FIG. 4. (a) Variation of the hole activity coefficient with hole concentration at 1000°C. (b) Variation of the Fermi level with hole concentration at 1000°C. The valence-band edge in pure GaAs is taken as $E_f=0$ and the energies within the band gap as negative.

and Eq. (9) may be written as

$$C_i=\gamma_p^2C_s^3/K_1p_{\mathrm{As}_4}^{1/4}, \tag{10}$$

where K_1 is a temperature-dependent constant.

With the condition $C_i \ll C_s$,[17] so that $C_s=C=p$, and the elimination of C_i from Eq. (7) by Eq. (10), the effective diffusion coefficient becomes

$$D=\frac{D_i}{K_1p_{\mathrm{As}_4}^{1/4}}C_s^2\gamma_p^2\left[\left(3+2\frac{C_s}{\gamma_p}\frac{d\gamma_p}{dC_s}\right)-\left(1+\frac{C_s}{\gamma_p}\frac{d\gamma_p}{dC_s}\right)\right]+D_s\left[1+\left(1+\frac{C_s}{\gamma_p}\frac{d\gamma_p}{dC_s}\right)\right]. \tag{11}$$

Equation (11) was written in the above form to emphasize that the term $[1+(C_s/\gamma_p)(d\gamma_p/dC_s)]$ represents the effect of the built-in field. Several treatments of diffusion in semiconductors have considered the field term for substitutional diffusion, and Smits[18] has obtained the above field term which gives an enhancement of D_s by a factor of 2 when γ_p is constant. Comparison of Eq. (11) with the experimental dependence of D on C_s in the following sections will permit neglect of the substitutional term.

[17] K. Weiser, J. Appl. Phys. 34, 3387 (1963).

[18] F. M. Smits, Ergeb. Exakt. Naturw. 31, 167 (1959).

B. Determination of the Diffusion Coefficient from the Diffusion Profiles

The Zn diffusion profile varies with time as $C_s=C_s(x/t^{1/2})$. Therefore, the diffusion coefficient at a given concentration may be obtained from the experimental $C_s(x)$ plot in Fig. 1 by the Boltzmann-Matano analysis.[2] This method makes a transformation in the one-dimensional diffusion equation and carries out the first integration. The resulting expression for the diffusion coefficient is

$$D_{C_x}=-1/(2t)\left[\int_0^{C_x} x dC_s/(dC_s/dx)_{C_x}\right]. \tag{12}$$

For a known diffusion time, the value of the diffusion coefficient D at a given concentration, $C_s=C_x$, is obtained by graphically evaluating the flux from 0 to C_x together with the concentration gradient at C_x. The resulting D-versus-C_s curve for 1000°C is shown in Fig. 3. A 1000°C isoconcentration point obtained with a pseudobinary source at $C_s=4\times10^{20}$ cm^{-3} is also given. At low concentrations both the slope and the $x\ dC_s$ in

the integral of Eq. (12) are difficult to evaluate, while at very high concentrations only the slope evaluation becomes a problem. Therefore, the greatest errors in the Boltzmann-Matano analysis occur at the lowest and highest concentrations. The data in Fig. 3 cover the range in C_s where these errors are least significant.

C. Determination of γ_p and E_f from the Concentration Dependence of the Diffusion Coefficient

The experimental variation of D with C_s shown in Fig. 3 indicates a concentration-squared dependence between 1 and 5×10^{19} cm^{-3} as previously reported.[1,4] In terms of Eq. (11), D will vary only as C_s^2 for a constant γ_p and a negligible D_s term. At the concentrations to be considered here, the substitutional term in Eq. (11) will be neglected and the effective diffusion coefficient may be written as

$$D=D^*C_s^2\gamma_p^2\left[1+\frac{C_s}{2\gamma_p}\frac{d\gamma_p}{dC_s}\right], \qquad (13)$$

where D^* is $2D_i/K_1p_{\mathrm{As}_4}^{1/4}$. The interpretation of the data in Fig. 3 will be based on Eq. (13).

At the lower concentrations, γ_p is unity[6] and D is simply $D^*C_s^2$. For higher concentrations, the experimental D increases more slowly than C_s^2 and even decreases. Finally, D again increases and, from the arguments of Ref. 6, γ_p approaches a constant value less than unity to give $D=D^*C_s^2\gamma_p^2$. The analysis of γ_p in Ref. 6 predicted a constant γ_p less than 1 at high concentrations, but theoretical arguments alone do not indicate the concentration range where the departure of γ_p from unity should begin. Interpretation of Fig. 3 in terms of Eq. (13) provides a means for determining the dependence of γ_p on C_s. The Fermi level is then found from Eq. (4) written as

$$\gamma_p=(A/p)\exp(E_f/kT), \qquad (14)$$

where A is a temperature-dependent constant which includes the reference potential energy E_0. The constant A may be evaluated by calculating E_f with the usual relationships,[19] utilizing the effective density of states and an ionization energy of 0 eV for concentrations above the intrinsic concentration, but where the Boltzmann statistics apply. The effective mass of holes has been taken as 0.68 and the band gap as $1.53-4.9\times10^{-4}\,T$ eV.[20]

Since γ_p enters Eq. (13) as $[\gamma_p^2+(C_s\gamma_p/2)(d\gamma_p/dC_s)]$, an explicit expression for γ_p cannot be obtained, and the values of γ_p as a function of C_s must be found by trial and error. The possible values of γ_p are further limited by imposing the restriction that the Fermi level is a single-valued, monotonic function of p. These restrictions mean that in the region where γ_p is less than 1, there is a minimum possible value of γ_p at any given C_s for E_f [given by Eq. (14)] to decrease smoothly. In the limiting case E_f becomes constant as C_s goes to larger concentrations. The γ_p and E_f curves shown in Figs. 4(a) and 4(b) were obtained in this manner from the solid curve in Fig. 3. The values calculated for the localized impurity level and impurity-band tailing along with the estimated transition region from Ref. 6 are also shown. It is readily seen that the limiting cases are in reasonable agreement, but the transition region was estimated (Ref. 6) to occur a decade too low in concentration.

[19] R. A. Smith, *Semiconductors* (Cambridge University Press, London, 1959), Chap. 4.

[20] H. Ehrenreich, Phys. Rev. **120**, 1951 (1960).

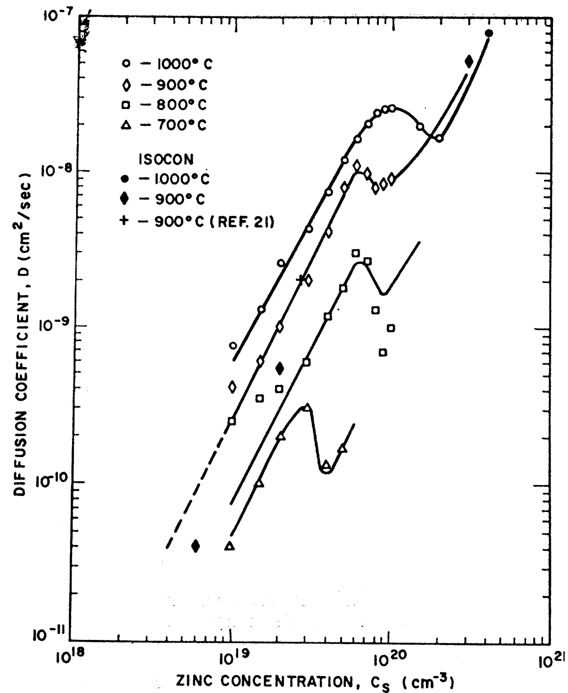

FIG. 5. Diffusion coefficient of Zn in GaAs versus Zn concentration at specified temperatures as derived from a Boltzmann-Matano analysis.

The diffusion coefficients as a function of concentration, as determined by Eq. (12) for a Boltzmann-Matano analysis, are given in Fig. 5 for the 1000, 900, 800, and 700°C profiles of Fig. 1. Isoconcentration diffusion coefficients taken from Refs. 8 and 21 at 900°C are shown for comparison. For each temperature the D-versus-C_s curve varies as C_s^2 at the lower concentrations, goes through a peak and a valley, and then increases. The γ_p and E_f at 900, 800, and 700°C were obtained from the D-versus-C_s curves in the manner described for the 1000°C curve. The resulting γ_p and E_f are shown in Fig. 6 and 7 along with the previous data for 1000°C.

IV. DISCUSSION

There are a number of features in both the diffusion analysis and the data represented in Figs. 5, 6, and 7 that require further discussion. The isoconcentration data tend to corroborate the values obtained from the

[21] D. L. Kendall (private communication).

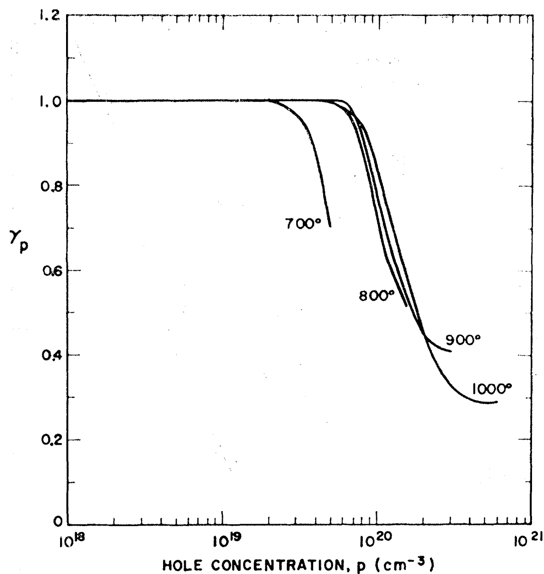

FIG. 6. Variaton of the hole activity coefficient with hole concentration at specified temperatures.

Boltzmann-Matano analysis, but there are differences that should be considered. Both the charge state of the species in the reaction of the interstitial Zn with a vacancy to form the substitutional Zn and maintenance of equilibrium must be questioned. From the present data together with other theoretical and experimental evidence discussed below, the interpretation of the variation of D with C_s as an experimental demonstration of the γ_p dependence on C_s is reasonably well substantiated.

Longini[3] suggested the diffusion by an interstitial-substitutional equilibrium because nearest neighbors of the Ga atoms are As atoms, and a substitutional Zn atom either has to diffuse into and out of an As vacancy or become interstitial to get to a neighboring vacancy in its own Ga sublattice. Regardless of the ionization state of the interstitial species for the interstitial-substitutional equilibrium diffusion, the effective diffusion coefficient at any temperature should vary inversely with the Ga vacancy concentration which is represented as a $p_{As_4}^{-1/4}$ dependence of D. Shih, Allen, and Pearson[22] studied the variation of D as a function of As_4 pressure and found that both the direction and the approximate magnitude of the dependence were correct. Chang[23] derived a theoretical expression for junction depth as a function of both time and temperature and found it agreed with the experimental results to further support the interstitial-substitutional model.

Correspondence between the theoretical and experimental D-versus-C_s dependence will be obtained if the local V_{Ga} equilibrium is essentially established, or if the concentration of V_{Ga} is essentially constant, but not for an intermediate situation. The observed correct D-versus-p_{As_4} dependence,[22] and the susceptibility of the experimental D-versus-C_s curves to interpretation in terms of Eq. (8) strongly suggest that the establishment of the vacancy equilibrium is rapid in comparison with the rate of Zn diffusion. The interpretation of the interstitial-substitutional equilibrium diffusion for Zn in GaAs is strongly supported by these observations.

The selection of the charge states for the species shown in Eq. (8) is based upon several considerations. The 1000°C solubility isotherm[6] could be only reasonably fit by a neutral Ga vacancy, and at the concentrations considered here the substitutional Zn is fully ionized.[6,10,11] The interstitial Zn has previously been considered either as a singly or doubly ionized donor. Longini[3] suggested doubly ionized because Zn normally loses two electrons in chemical bonding, but Weisberg and Blanc[4] pointed out that the second ionization potential (in vacuum) of Zn (17.9 eV) exceeds the first potential of hydrogen (13.5 eV) and is close to the second ionization for copper (20.3 eV). Since in GaAs hydrogen is neutral, while interstitial Cu is a single donor, Weisberg and Blanc concluded that interstitial Zn is probably a single donor.[4] Wiser[17] assumed the interstitial Zn was a singly ionized donor by combining experimental data for Cu in GaAs with theories of solubility and diffusion of interstitial impurities and obtained reasonable order-of-magnitude estimates of D. A diffusion and electrical transport study of Zn in InAs by Boltaks and Rembeza[24] was interpreted to indicate that the interstitial Zn was doubly ionized. However, they did not consider that D varies with concentration and As pressure as well as temperature, which makes their interpretation questionable without further information. If the interstitial Zn was taken as doubly ionized, then the effective diffusion coefficient would be

$$D=\tfrac{3}{2}D^*C_s^3\gamma_p^3\left[1+\frac{2}{3}\frac{C_s}{\gamma_p}\frac{d\gamma_p}{dC_s}\right], \qquad (15)$$

and would vary as the concentration cubed at low concentrations. Because our data indicate a concentration-squared dependence at low concentrations, and Weisberg and Blanc[4] were able to regenerate Cunnell and Gooch's[1] diffusion profiles with the concentration-squared dependence, we have taken the interstitial species as singly ionized.

The D from the Boltzmann-Matano analysis and the isoconcentration D have at least two basic differences. For the isoconcentration diffusion,[7,8] nonradioactive Zn (as pure Zn or a Zn-Ga source) is first diffused into the sample for a sufficiently long time to obtain a uniform Zn concentration through the entire sample. The sample is then diffused with radioactive ^{65}Zn and the nonradiative Zn diffuses out while the ^{65}Zn diffuses in. The total Zn concentration throughout remains constant at all times. The resulting ^{65}Zn profile is a complementary error function which readily permits

[22] K. K. Shih, J. W. Allen, and G. L. Pearson, Bull. Am. Phys. Soc. **10**, 1180 (1965).
[23] L. L. Chang, Solid State Electron. **7**, 853 (1964).
[24] B. I. Boltaks and S. I. Rembeza, Fiz. Tverd. Tela **8**, 2649 (1966) [English transl.: Soviet Phys.—Solid State **8**, 2117 (1967)].

determination of D at the fixed isoconcentration level. Since the total Zn concentration is constant, the field term in Eq. (11) for the effective diffusion coefficient is zero. The effective diffusion coefficient for the isoconcentration diffusion D_{isocon} (neglecting the D_s term) is

$$D_{\text{isocon}}=D^*C_s^2\gamma_p^2\left[\frac{3}{2}+\frac{C_s}{\gamma_p}\frac{d\gamma_p}{dC_s}\right], \qquad (16)$$

which differs slightly from Eq. (13) which includes the field term. In the low- and very high-concentration range $D=2D_{\text{isocon}}/3$, so that at a given concentration D_{iscocon} would be greater by $\frac{3}{2}$ because the interstitial diffusion is not retarded by the field. Because the term D^* in Eqs. (13) and (16) contains $p_{\text{As}_4}{}^{-1/4}$, it is necessary to take into account the decreased As pressure for the isoconcentration diffusions of Ref. 8 at surface concentrations less than the pseudobinary value. These As pressure considerations mean that D_{isocon} should be greater than D at the same concentration. In Fig. 5 D_{isocon} and D are about the same, near 2 to $3\text{x}10^{19}$ cm^{-3}, but D_{isocon} is much less than the extrapolated D at 5×10^{18} cm^{-3}. If the isoconcentration data points are fit, a D variation as C_s^3 is necessary as given by Eq. (15) for doubly ionized interstitial Zn. There may be other factors that make D differ from D_{isocon}. For our present purposes, the isoconcentration data are taken as guidelines that the values assigned to D from the Boltzmann-Matano analysis are representative of the diffusion process being analyzed. An attempt to reconcile the isoconcentration and Boltzmann-Matano data probably should not be attempted without more extensive experimental data.

It has been suggested that the precipitation of Zn during diffusion should be considered in the analysis of the diffusion process.[25] Although it has been demonstrated that dislocations can form in the diffused layer under certain diffusion conditions,[25,26] it is difficult to demonstrate that the dislocation formation is accompanied by Zn precipitation. Even with the observance of precipitated Zn, it would not be clear whether or not the Zn precipitated during diffusion or during cooldown because Zn can move so rapidly. High concentrations of Zn in the presence of dislocations have not led to measurable discrepancies between the total Zn concentration and the hole concentration.[6,10,11] If sufficient amounts of precipitation occurred, so that the equilibrium expressed by Eq. (8) was not representative of this system, then the maximum solubilities obtained from diffusion should exceed the equilibrium solubility found in the grown crystals. This was not the case. For these reasons, it is not necessary to include precipitation in the diffusion analysis.

In Fig. 5 the D-versus-C_s curves for each temperature display the same general features of a C_s^2 dependence at low concentrations, a peak and a valley, and then again an increase. The concentrations at which the peak and the valley occur appear to move to higher concentrations as the temperature increases. However, roughness of the experimental data precludes obtaining a smooth trend. This trend is more noticeable for the D versus C_s of Zn in GaP shown in Fig. 2 of Ref. 13. The data points for 8, 9, and 10×10^{19} cm^{-3} at 800°C cannot be fit without permitting E_f to have a nonmonotonic dependence on concentration. The solid curve at 800°C was drawn for the limiting case of E_f constant with C_s, and is more in line with the ratio of D at the peak to D at the valley obtained at the other temperatures. Some roughness of the data is again apparent in Figs. 6 and 7, but the general features of a departure in γ_p from 1 and a decrease in the variation of E_f with C_s in the concentration range where D departs from a C_s^2 dependence is clear.

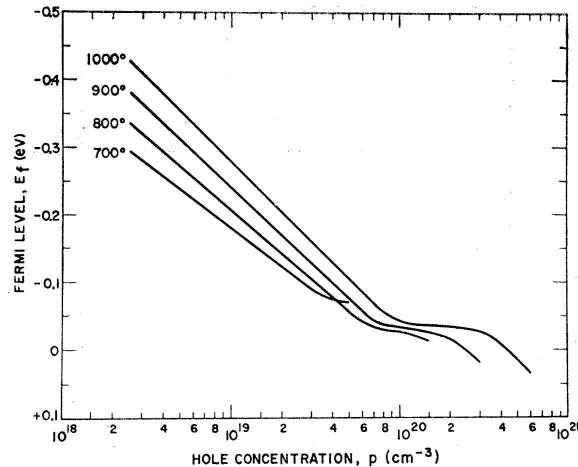

FIG. 7. Variation of the Fermi level with hole concentration at specified temperatures. The valance-band edge in pure GaAs is taken as $E_f=0$ and the energies within the band gap as negative.

In fact, in terms of Eq. (13) the initial departure from the C_s^2 dependence indicates the concentration where γ_p becomes less than unity. The valley in the D-versus-C_s curve occurs approximately at the inflection point of the linear γ_p-versus-C_s plot. The approach again of D to a C_s^2 dependence indicates γ_p is again approaching a constant value, but for γ_p less than unity.

Introduction of γ_p obtained from the D-versus-C_s curve into the previous solubility analysis[6] provides verification of the γ_p and E_f concentration dependence that has been presented here. The substitutional Zn concentration was related to the atom fraction of Zn in the liquid $X_{\text{Zn}l}$ by Eq. (5) of Ref. 6,

$$C_s=(K\gamma_{\text{Zn}l}X_{\text{Zn}l}\gamma_{\text{As}l}X_{\text{As}l}/\gamma_p)^{1/2}, \qquad (17)$$

where K is a constant dependent only on temperature, $\gamma_{\text{Zn}l}$ the activity coefficient of Zn in the liquid, $\gamma_{\text{As}l}$ the activity coefficient of As in the liquid, and $X_{\text{As}l}$ the atom fraction of As in the liquid. Incorporation of the 1000°C γ_p values given in Fig. 4(a) into Eq. (17) along with the previous values[6] of $\gamma_{\text{Zn}l}$ $X_{\text{Zn}l}$ and $\gamma_{\text{As}l}$ $X_{\text{As}l}$

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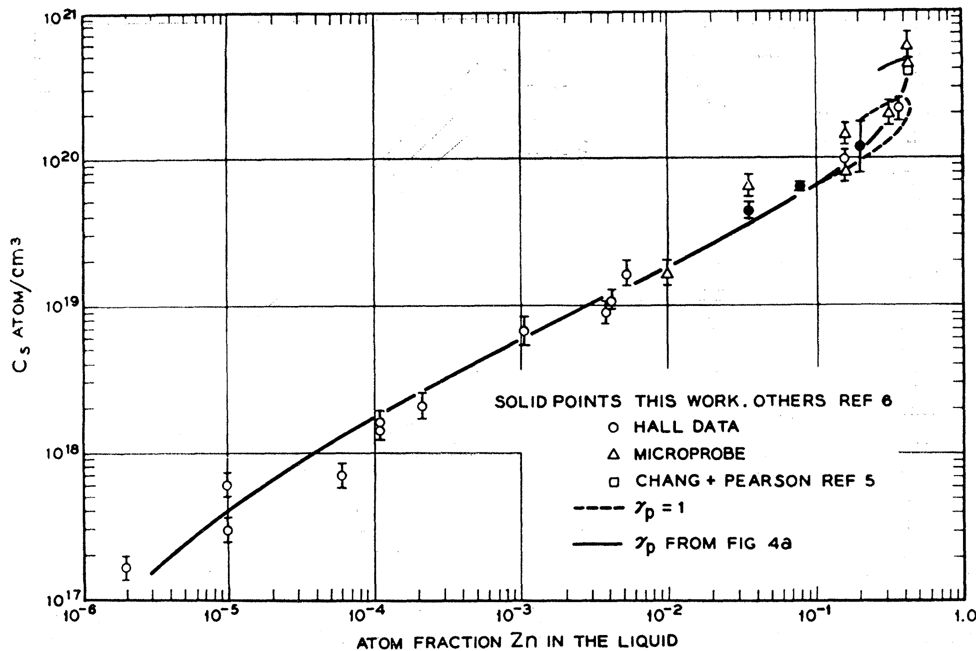

FIG. 8. The Ga branch of the 1000°C solid-solubility isotherm.

results in the C_s-versus-$X_{\mathrm{Zn}l}$ curve shown in Fig. 8. The curve for a unity γ_p has been included to indicate that the experimental data require γ_p to become less than unity at high concentrations. Comparison of the experimental and calculated C_s, which tests the C_s dependence of γ_p, can be made over the entire concentration range by considering only the Ga-rich region of the phase diagram as shown. On the As-rich side the $\gamma_{\mathrm{Zn}l}$ values are presently somewhat uncertain. Determination of $\gamma_{\mathrm{Zn}l}$ in this region is presently being investigated and comparison of the experimental and calculated C_s on the As-rich side will be made when these data are available. Since the curve in Fig. 8 did not pass through the previous[6] data points at $X_{\mathrm{Zn}l}=3.5\times10^{-2}$ and 1.5×10^{-1}, additional samples were prepared and analyzed. These new data points have been included with the previous data of Fig. 2 of Ref. 6 and more clearly define the experimental behavior of C_s. Within the range of scatter and uncertainty of the experimental C_s data, a reasonable fit of the calculated C_s will occur only for γ_p values within a narrow range of those given in Fig. 4(a). Because the γ_p represented here will explain two independent experiments, the variation of D with C_s and the solid solubility isotherm of Fig. 8, strong justification of the interpretation of diffusion as presented here does result. This analysis is also readily applicable to diffusion of Zn in GaP,[13] where similar dependence of D on C has been observed. The higher Zn concentrations in InP [27] and InAs [28] require consideration of more complex reactions.

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V. CONCLUSION

Dependence of the Zn diffusion coefficient D in GaAs on the Zn concentration C_s, as obtained from experimental diffusion profiles by a Boltzmann-Matano analysis, has been explained in terms of the interstitial-substitutional equilibrium diffusion. This interpretation leads to the conclusion that the departure of D from a C_s^2 dependence is due to the hole-activity coefficient γ_p becoming less than unity at high Zn (hole) concentrations. At the highest concentrations the Fermi level E_f obtained from γ_p agrees with E_f calculated from the model of Halperin and Lax, which considers the effect of the high impurity density on the density of states. In the dilute concentration range where a localized impurity level is applicable and in the high-concentration range of impurity-band tailing, theoretical calculations can provide limiting values of E_f and γ_p, while the experimental D-versus-C_s data provide the detailed behavior between these limiting values. At 1000°C the localized level applies for concentrations below $C_s \simeq 4\times10^{19}$ cm^{-3} and the impurity-band tailing applies above 3×10^{20} cm^{-3}.

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