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An Analysis of Diffusion in Semiconductors

Abstract: In the experimental determinations of the coefficients of diffusion of impurities in semiconductors reported to date, it has usually been assumed that these coefficients do not vary with concentration. This assumption is questioned here. Interactions between acceptors, donors, electrons, and holes may lead to complicated diffusion equations, as shown by an analysis based on Onsager's theory. In particular, appreciable covalent compound formation is likely to occur between some substitutional donors and acceptors. This alone may lead to a marked dependence of diffusion coefficients on concentration, and to diffusion of acceptors induced by concentration gradients of donors and vice versa. Such effects are suggested by some discrepancies in the experimental results reported thus far.

Introduction

The increasing interest of the electronics industry in graded-base transistors has prompted intensive studies on the diffusion of impurities into semiconductors.[1,2] Since the distribution of impurities in the graded base affects the transistor characteristics, it is desirable to estimate and control the diffusion pattern with the highest possible accuracy.

It has been frequently taken for granted that the diffusion rate is governed by Fick's laws:[3]

$$J = -D(\partial n/\partial x) \tag{1}$$

$$\text{and } (\partial n/\partial t)_x = -(\partial J/\partial x)_t \tag{2a}$$

$$= D(\partial^2 n/\partial x^2)_t \tag{2b}$$

Where J is the current and n the concentration of a diffusing substance, D a diffusion coefficient, t the time, and x the distance. For the sake of conciseness, only unidirectional diffusion is considered here.

It is known, however, that Eqs. (1) and (2b) do not hold for many systems. A more widely applicable relation, first used by Boltzmann,[4] takes account of any possible variations of the diffusion coefficient D with concentration:

$$\partial n/\partial t = D(n)(\partial^2 n/\partial x^2) + (\partial D(n)/\partial n)(\partial n/\partial x)^2 \tag{3}$$

where $D(n)$ is a function of concentration. Equation (3) follows directly from Eq. (2a) and the generalized form of Eq. (1):

$$J = -D(n)(\partial n/\partial x) \tag{4}$$

An obvious extension of Eq. (3) to systems of more than two components is:

$$\partial n_i/\partial t = D_i(n)(\partial^2 n_i/\partial x^2) + \Sigma_j[(\partial D_i(n)/\partial n_j)(\partial n_i/\partial x)(\partial n_j/\partial x)] \tag{5}$$

where the subscripts i, j, refer to the various components. Equation (5) probably could be made to fit most experimental data available to date, since the function $D_i(n)$ can be adjusted at will. The experimental problem would then consist simply of determining $D_i(n)$ over all conceivable ranges. Since this would require a tremendous amount of work, it is usually preferred to assume at first that $D_i(n)$ may be represented by a constant D. This expedient assumption may be quite satisfactory when high accuracy is either unnecessary or unattainable.

Unfortunately, however, the accuracy attainable by an experimental procedure is frequently judged solely by the consistency of the results obtained. Rather than attribute any observed discrepancies to actual variations in $D_i(n)$, one may be tempted, instead, to blame them on possible experimental errors.

The present paper will be concerned with the applicability of Fick's law, Eq. (2b), to the diffusion of acceptors and donors into semiconductors. It will be shown that, theoretically, this law may not apply if compound formation or other complicating factors are significant. This proof will be followed by a discussion of some experimental work reported to date.

Onsager's equations for isothermal diffusion

A theoretical approach quite generally applicable to isothermal diffusion is due to Onsager.[5] His equations are:

$$Ji = -\Sigma_j \Omega_{ij} \partial \mu_j/\partial x - \Omega_i f_i \tag{6}$$

where μ_j is the chemical potential of the *j-th* component, f_i the average resultant force due to any electrical or other fields acting on a particle of the *i-th* species, and Ω_{ij} are mobility terms obeying the reciprocity relation:

$$\Omega_{ij} = \Omega_{ji} \tag{7}$$

The term Ω_{ii} is proportional to the concentration n_i of the particles of the *i-th* species and inversely proportional to the frictional forces opposing the displacement of these particles. Where these frictional forces are approximately invariant this can be written:

$$\Omega_{ii} \simeq n_i D_i / kT \tag{8}$$

where T is the absolute temperature, k the Boltzmann constant, and D_i the diffusion coefficient. For nearly ideal solutions the chemical potential is:

$$\mu_i \simeq RT \ln n_i \tag{9}$$

and

$$\partial \mu_i / \partial x \simeq (RT/n_i)(\partial n_i / \partial x) \tag{10}$$

Hence, if the terms $\sum_{i \neq j} \Omega_{ij}(\partial \mu_j / \partial x)$ and f_i are negligible, Eq. (6) reduces to Eq. (1).

The terms Ω_{ij} where $i \neq j$ may be much more complicated. To obtain a physical picture of their meaning, one might consider the simple case where two components A and B form compound C:

$$A + B \rightleftarrows C$$

and where the motions of the individual species A, B, and C *are not otherwise interrelated.* Then the condition for local equilibrium is:

$$\mu_A + \mu_B = \mu_C \tag{11}$$

If Eq. (6) were then to describe the motion of the total substance A, it could be written:

$$-J_A \cong \Omega^*_{AA}(\partial \mu_A / \partial x) + \Omega_{CC}(\partial \mu_C / \partial x) \tag{12}$$

where Ω^*_{AA} and Ω_{CC} are given by Eq. (8):

$${}_A D^*_A / kT \Omega^*_{AA} = n^* \quad \text{and} \quad \Omega_{CC} = n_C D_C / kT, \tag{13}$$

where D^*_A and n^*_A apply to that part of substance A which is not combined. If it is not desired, however, to consider the combined and uncombined forms separately, then Eq. (6) would be written:

$$-J_A = \Omega_{AA}(\partial \mu_A / \partial x) + \Omega_{AB}(\partial \mu_B / \partial x) \tag{14}$$

Comparison of Eqs. (11), (12) and (14) lead to

$$\Omega_{AB} = \Omega_{CC} \tag{15}$$

and $\Omega_{AA} = \Omega^*_{AA} + \Omega_{CC}$

In more complicated cases, however, the terms Ω_{ij}, where $i \neq j$, may be due to either an entrainment or an obstruction of the *i-th* species by the *j-th* species, or vice versa, through long-range interactions.

The following sections will be concerned with the application of Onsager's equations to diffusion of donors and acceptors into semiconductors under conditions where simplified treatments may be legitimate. These conditions will be specified in the next section.

Complicating factors in the theoretical treatment of diffusion in semiconductors

According to Longini and Greene[6] the concentration of vacancies in semiconductors may be highly dependent on the difference between the concentrations of donor and acceptor impurities, and would be much higher for n-type than for p-type semiconductors. In such cases the coefficient D_i of equation (8) would have to be replaced by a function $D_i(n_i, n_j \ldots)$ of the concentrations, as diffusion of substitutional impurities is believed to be determined by the vacancy concentration. *This possibility would introduce further complications, which though important, are outside the scope of the present paper.*

Since donor and acceptor impurities are almost completely ionized at temperatures at which appreciable diffusion occurs, their chemical potentials are affected by complex electrostatic interactions, such as those described by Reiss et al.[7] Fortunately, however, these interactions decrease with increasing concentration and increasing temperature. Furthermore, at temperatures for which the concentration of electrons and holes in the intrinsic semiconductor is higher than the impurity concentration, any variation of the latter will have a negligible effect on the observable electrostatic contributions to chemical potentials. This range of temperatures and concentrations will therefore be considered exclusively in the following sections.

Finally, it will be assumed that any entrainment of particles of one species by those of another species is negligible in solid semiconductors. However, space-charge effects will be considered.

Summarizing, then, the following treatment will apply to conditions for which equations (8) and (10) would apply to each impurity species and where the terms Ω_{ij} are negligible for $i \neq j$.

Electrical field associated with impurity concentration gradients

When different species of charged particles are diffusing, those having high mobilities tend to advance ahead of the remaining species. This tendency, however, is checked by the requirement for electroneutrality if the fast and slow particles are oppositely charged. Thus a space-charge field is formed which accelerates the slower particles and retards the fast ones. To estimate the effect of this field, consider a semiconductor with the concentrations N and P of donor and acceptor impurities, re-

spectively, at a given absolute temperature T. The concentrations n_e and n_h of electrons and holes, respectively, will then be determined by the electroneutrality condition

$$n_e - n_h = N - P \tag{16}$$

and by the mass action law

$$n_e n_h = K_1 \tag{17}$$

where K_1, is a constant. Let D_N, D_P, D_e, and D_h be the diffusion coefficients for donors, acceptors, electrons, and holes, respectively. Then, Eqs. (6), (8) and (10) yield

$$J_N = -D_N[(\partial N/\partial x) + NF/kT] \tag{18}$$

$$J_P = -D_P[(\partial P/\partial x) - PF/kT] \tag{19}$$

$$J_e = -D_e[(\partial n_e/\partial x) - n_e F/kT] \tag{20}$$

$$\text{and } J_h = -D_h[(\partial n_h/\partial x) + n_h F/kT] \tag{21}$$

where J_N, J_P, J_e and J_h are the respective diffusion currents of donors, acceptors, electrons, and holes, and $-F$ is the average electrical force acting on a positively charged particle. The cross terms $\Omega_{ij}(\partial\mu_j/\partial x)$ of equation (6) where $i \neq j$ are assumed to be negligible. In the absence of any net electrical current one must have:

$$J_N + J_h = J_P + J_e \tag{22}$$

as long as no appreciable local deviations from electroneutrality occur.

Eqs. (16) through (22) allow calculation of F in terms of P, N, $\partial P/\partial x$, and $\partial N/\partial x$. From Eqs. (16) and (17) one obtains:

$$n_e = \tfrac{1}{2}(N-P) + [\tfrac{1}{4}(N-P)^2 + K_1]^{\frac{1}{2}} \tag{23}$$

$$n_h = -\tfrac{1}{2}(N-P) + [\tfrac{1}{4}(N-P)^2 + K_1]^{\frac{1}{2}} \tag{24}$$

$$\partial n_e/\partial(N-P) = \tfrac{1}{2}[1+(N-P)/(\tfrac{1}{4}(N-P)^2 + K_1)^{\frac{1}{2}}] \tag{25}$$

$$\text{and } \partial n_h/\partial(N-P) = \tfrac{1}{2}[-1+(N-P)/(\tfrac{1}{4}(N-P)^2 + K_1)^{\frac{1}{2}}] \tag{26}$$

For $K_1 >> (N-P)^2$, equations (23) through (26) simplify to:

$$n_e \simeq n_h \simeq \sqrt{K_1} \tag{27}$$

$$\text{and } \partial n_e/\partial(N-P) \simeq -\partial n_h/\partial(N-P) \simeq \tfrac{1}{2} \tag{28}$$

$$\text{Hence, } \partial n_e/\partial x = [\partial n/\partial(N-P)][\partial(N-P)/\partial x] \simeq \tfrac{1}{2}\,\partial(N-P)/\partial x \tag{29}$$

$$\text{and } \partial n_h/\partial x \simeq -\tfrac{1}{2}\,\partial(N-P)/\partial x \tag{30}$$

Substitution of Eqs. (27) through (30) in Eqs. (20) and (21), followed by substitution of the latter together with Eqs. (18) and (19) into Eq. (22), then yields:

$$D_N\left[\frac{\partial_N}{\partial x} + \frac{NF}{kT}\right] + D_h\left[-\tfrac{1}{2}\frac{\partial(N-P)}{\partial x} + \frac{\sqrt{K_1}F}{kT}\right] = D_P\left[\frac{\partial_P}{\partial x} - \frac{PF}{kT}\right] + D_e\left[\tfrac{1}{2}\frac{\partial(N-P)}{\partial x} - \frac{\sqrt{K_1}F}{kT}\right] \tag{31}$$

$$\text{Hence, } \frac{F}{kT} = \frac{\tfrac{1}{2}(D_e+D_h)(\partial(N-P)/\partial x) + D_P(\partial P/\partial x) - D_N(\partial N/\partial x)}{\sqrt{K_1}(D_e+D_h) + ND_N + PD_P} \tag{32}$$

Since D_e and D_h are much larger than D_P and D_N, equation (30) simplifies to:

$$F/kT \simeq [\partial(N-P)/\partial x]/2\sqrt{K_1} \tag{33}$$

Hence, Eqs. (18) and (19) become:

$$J_N = -D_N[(1+\tfrac{1}{2}NK_1^{-\frac{1}{2}})(\partial N/\partial x) - \tfrac{1}{2}NK_1^{-\frac{1}{2}}(\partial P/\partial x)] \tag{34}$$

and

$$J_P = -D_P[(1+\tfrac{1}{2}PK_1^{-\frac{1}{2}})(\partial P/\partial x) - \tfrac{1}{2}PK_1^{-\frac{1}{2}}(\partial N/\partial x)] \tag{35}$$

Effect of compound formation

It has been pointed out by Reiss, Fuller and Morin[7] that the electrostatic attraction between the positively charged donor particles and the negatively charged acceptors should give rise to ion-pairing:

$$D^+ + A^- \rightleftharpoons AD$$

Their theoretical treatment of such pairing was based mainly on electrostatic considerations. However, covalent interactions and geometric factors affecting the stability of the crystal lattice may be stronger contributing factors towards such pairing than purely electrostatic attraction, especially in the case of substitutional impurities, e.g., indium and antimony in germanium or silicon. Covalent compounds such as InSb, AlSb, etc., are known to be very stable, as evidenced by their negative energies of formation.[8,9] It is very likely, then, that even in a crystal of germanium or silicon, strong covalent forces will favor such compound formation. Furthermore, the negatively charged acceptors usually have a larger effective radius and the positively charged donors a smaller one, than does a neutral germanium or silicon atom. Hence, substitution of a germanium or silicon atom by

an acceptor or donor may produce a local compression or contraction of the lattice. When a donor and acceptor are placed in adjacent lattice sites, these local strains should be largely relieved and appreciable energy thus released.*

The fraction of donors and acceptors which are paired would be a complicated function of their concentrations if electrostatic interaction energies were the controlling factors, but this function would assume a simple form if short-range covalent and intracrystalline energies are mainly involved. In the latter case, the simple equilibrium relation should hold:

$$K_2 \simeq N^*P^*/C \tag{36}$$

where K_2 is an equilibrium constant, C is the concentration of the compound AD, and N^* and P^* are the concentrations of free donors and acceptors, respectively, i.e., of those donors and acceptors which are not in combined form. Hence, at equilibrium:

$$dC = (P^*/K_2)dN^* + (N^*/K_2)dP^* \tag{37}$$

If the local rate of attainment of equilibrium is fast in comparison with the rate of diffusion, then C could be considered to follow instantaneously any local changes in N^* and P^* so that

$$(\partial C/\partial t)_x \simeq (P^*/K_2)(\partial N^*/\partial t)_x + (N^*/K_2)(\partial P^*/\partial t)_x \tag{38}$$

Hence, if J_N^* and J_P^* are the diffusion currents of free donors and acceptors, the continuity Eq. (2a) would no longer apply,

$$(\partial N^*/\partial t)_x \neq -(\partial J_N/\partial x)_t$$

$$(\partial P^*/\partial t)_x \neq -(\partial J_P/\partial x)_t$$

but would have to assume the form

$$(\partial N^*/\partial t)_x = -(\partial J_N/\partial x)_t - (\partial C/\partial t)_x \tag{39}$$

$$(\partial P^*/\partial t)_x = -(\partial J_P/\partial x)_t - (\partial C/\partial t)_x \tag{40}$$

where the correction term $-(\partial C/\partial t)_x$ would represent the concentration of donors or acceptors changing into the compound AD. Any diffusion of compound AD itself is disregarded here, because its diffusion coefficient should be extremely small, in view of its larger size and weight, and, what is probably most important, its tighter bonding in the crystal lattice.

Eqs. (39) and (40) yield:

$$(\partial P^*/\partial t)_x = (\partial N^*/\partial t)_x + (\partial J_{N^*}/\partial x)_t - (\partial J_{P^*}/\partial x)_t \tag{41}$$

Eliminating $(\partial P^*/\partial t)_x$ and $(\partial C/\partial t)_x$ between Eqs. (38), (41), and (39), and rearranging, one obtains:

$$(\partial N^*/\partial t)_x = [1/(K_2+N^*+P^*)]$$
$$[N^*(\partial J_{P^*}/\partial x)_t - (K_2+N^*)(\partial J_{N^*}/\partial x)_t] \tag{42}$$

Similarly,

$$(\partial P^*/\partial t)_x = [1/(K_2+N^*+P^*)]$$
$$[P^*(\partial J_{N^*}/\partial x)_t - (K_2+P^*)(\partial J_{P^*}/\partial x)_t] \tag{43}$$

where the terms $\partial J/\partial x$ would be given by substituting the letters N^* and P^* for N and P in Eqs. (34) and (35).

Discussion of the derived relations

Even if no compound formation occurred, it follows from Eqs. (34) and (35) that, strictly speaking, diffusion in semiconductors should fail to obey not only Fick's laws, but also the more generalized Eqs. (4) and (5). In order to hold strictly, the latter equations would have to be generalized even further:

$$J_i = -\Sigma_j D_{ij}(n)(\partial n_j/\partial x) \tag{44}$$

Comparing Eqs. (34) and (35) with (44) one obtains:

$$D_{NN} = (1+\tfrac{1}{2}NK_1^{-\frac{1}{2}})D_N \tag{45}$$

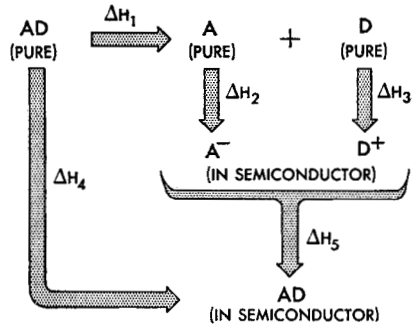
$$D_{PP} = (1+\tfrac{1}{2}PK_1^{-\frac{1}{2}})D_P \tag{46}$$

$$D_{NP} = -\tfrac{1}{2}NK_1^{-\frac{1}{2}}D_N \tag{47}$$

and $$D_{PN} = -\tfrac{1}{2}PK_1^{-\frac{1}{2}}D_P \tag{48}$$

Since it has been assumed in this discussion that $N<K_1^{\frac{1}{2}}$ and $P<K_1^{\frac{1}{2}}$, D_{NN} and D_{PP} cannot vary by a factor greater than 3/2 over the entire range of concentrations considered. Furthermore, in most practical cases encountered, $N \ll K_1^{\frac{1}{2}}$ and $P \ll K_1^{\frac{1}{2}}$, so that D_{NN} and D_{PP} reduce to D_N and D_P, respectively. However, the terms

*Consider, e.g., the cycle:



The energy change ΔH_5 would then be:

$$\Delta H_5 = \Delta H_4 - (\Delta H_1 + \Delta H_2 + \Delta H_3)$$

Now the low solubilities of uncompensated acceptors A and donors D as compared with those of many AD compounds in semiconductors suggest that usually $\Delta H_2 > \Delta H_4$ and $\Delta H_3 > \Delta H_4$. Hence, ΔH_5 may have appreciable negative values, a major fraction of which may be attributed to the forces discussed above.

$D_{NP}\partial P/\partial x$ and $D_{PN}\partial N/\partial x$ appearing in Eq. (44) may not be negligible in certain cases. Thus, if the gradient of one impurity species is zero, while that of the other is high, these terms predict counterdiffusion of the former species in the direction of increasing concentration of the latter.

Much larger deviations from Fick's law would occur, however, in case of appreciable compound formation, as shown by Eqs. (42) and (43). In the extreme case where K_2 is negligibly small, compound formation would be stoichiometric, and Eqs. (42) and (43) would reduce to:

$$\partial N^*/\partial t = -\partial J_{N^*}/\partial x \qquad \text{for } N>P \qquad (49a)$$

$$= 0 \qquad \text{for } N\leqslant P \qquad (49b)$$

$$\partial P^*/\partial t = -\partial J_{P^*}/\partial x \qquad \text{for } N<P \qquad (50a)$$

$$= 0 \qquad \text{for } N\geqslant P \qquad (50b)$$

Eqs. (49) and (50) could be rewritten in terms of the *excess* donor or acceptor concentrations:

$$\partial(N-P)/\partial t = -\partial J_{N^*}/\partial x \qquad \text{for } N>P \qquad (51a)$$

$$= +\partial J_{P^*}/\partial x \qquad \text{for } P>N \qquad (51b)$$

The problem would then be similar to that for diffusion in a two-phase system, and solutions worked out for the latter case could be applied here.[10] The result would be a sharp change in $\partial(N-P)/\partial x$ for $N = P$, i.e., at the $p-n$ junction.

The actual existence of sharp changes in $\partial(N-P)/\partial x$ would be indicated by the lines observed when germanium crystals are cross sectioned and etched following diffusion of impurities. The locations of such etchlines do not always coincide, however, with those of the $p-n$ junction.[11] Nevertheless, the etchlines suggest irregularities in concentration gradients which could not be predicted by Fick's law. On the other hand, when K_2 is not quite negligible, Eqs. (42) and (43) may lead to steep changes in $\partial(N-P)/\partial x$ at points which do not necessarily coincide with the $p-n$ junction. Similar irregularities might also occur even if K_2 is negligibly small, but where the equilibrium between the concentrations of free and of paired impurities is attained rather slowly.

Experimental evidence of pairing between acceptors and donors and of its effect on diffusion is given by Reiss et al[7] for boron and lithium in silicon. This pairing is, however, mainly attributed to electrostatic interactions and the formation of an LiB^- complex. Since lithium is an interstitial rather than substitutional impurity, it may well be that these interactions are more significant in this case than the covalent and intracrystalline interactions discussed in the previous section.

In most of the other experimental work on diffusion in semiconductors, Fick's law was assumed to be valid, and any discrepancies were attributed to experimental error. Some of these might be due, however, to the complicating factors discussed above. Thus, in Dunlap's work[1] on the diffusion of antimony into germanium, the diffusion coefficients obtained by the tracer method were consistently higher than those given by the $p-n$ junction method. This result could suggest counterdiffusion of acceptors due partly to electrical fields, Eqs. (34) and (35), but mainly to compound formation, Eqs. (42) and (43).

Discrepancies between results of different investigators[1,12] might perhaps be also attributed partly to differences in the concentrations of the diffusing impurities and of the impurities initially present in the semiconductors in the different experiments. The same might apply to some discrepancies between values obtained by the same authors. Unfortunately, the *a priori* assumption of the validity of Fick's law has led to a common failure to report accurately the impurity contents of the specimens studied. In particular, the concentrations of the impurities present in these samples prior to diffusion have rarely been mentioned.

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