conductivity $\eta_a w_0$ only begins to reflect the rise in mobility as the temperature is lowered because of the existence of shallow traps in the crystals studied to date. These traps are most effective at temperatures below 25°K where the mobility has leveled off. It seems reasonable that these defects are scattering as well as trapping centers at low temperature. One might inquire as to the relative probability for scattering as compared to that for trapping. For most defects in semiconductors, the scattering cross section is larger than the trapping cross section.[16] A comparison below 25°K in the present case gives the trapping time $\tau_t = w_0/\mu \simeq 1.5\times10^{-10}$ sec ($w_0 \approx 6\times10^{-7}$ cm$^2$/volts[1]) whereas the scattering time is of the order of magnitude $\tau = \mu m/e = 2.5\times10^{-12}$ sec. The difference seems large enough to justify our interpretation of the transient Hall experiment in terms of mobility and relaxation time $\tau$.

It would be interesting to pursue the matter of the relative scattering and trapping times further, perhaps by a direct measurement of trapping time as a function of temperature. Several other points for future study suggest themselves. For example, it is important to improve the accuracy and extend the Hall measurements to other alkali halides having different coupling strengths and Reststrahl wavelengths. The origin of the scattering below 30°K is unknown but it would be interesting to see if the residual mobility can be increased by crystal purification as has been found to be the case for the silver halides.

---

[16] M. Lax, Phys. Rev. **119**, 1502 (1960).

---

PHYSICAL REVIEW VOLUME 121, NUMBER 5 MARCH 1, 1961

# Diffusion in Compound Semiconductors*

B. Goldstein
*Radio Corporation of America Laboratories, Princeton, New Jersey*

(Received September 27, 1960)

Self-diffusion in single crystal InP and GaAs has been measured, together with the diffusion of the acceptors Cd and Zn and the donors S and Se in GaAs. Radioactive isotopes of these elements were used as tracers. The diffusions of In and P in InP are characterized by activation energies of 3.85 ev and 5.65 ev, respectively; those for Ga and As in GaAs are characterized by activation energies of 5.60 ev and 10.2 ev, respectively. The marked differences in both activation energies and diffusion rates of the constituent atoms in these materials indicate that the basic mechanism of the self-diffusion is one of migration within a specific sublattice.

The impurity diffusion measurements in GaAs suggest that the concept of sublattice diffusion be extended to include impurity diffusion when the impurities enter the lattice substitutionally. The activation energy of the diffusion of both Cd and Zn in GaAs is about 2.5 ev, while that of the diffusion of both S and Se in GaAs is about 4.1 ev. Experimental details of interest include the observation of GaS compound formation when GaAs is heated in S vapor, and the formation of glassy layers on the surface of GaAs due to Se.

## I. INTRODUCTION

THIS paper presents and discusses measurements of self-diffusion in single crystal indium phosphide and gallium arsenide and the diffusion of cadmium, zinc, sulfur, and selenium in GaAs. Radioactive isotopes of these elements were used as tracers. The work was undertaken to determine primarily the diffusion constants and activation energies, and by so doing to determine, if possible, the specific mechanism of the diffusion in these materials.

InP and GaAs belong to the class of intermetallic compound semiconductors comprised of elements from columns IIIb and Vb of the periodic table. The properties of these materials which make them interesting as host matrices for diffusion studies are (1) their structure, which consists of two interpenetrating face centered cubic lattices, each of which is composed of one of the constituent atomic species, (2) the stoichiometry of the constituent atoms which is better than 1 part in $10^5$, and (3) the fact that their electrical properties provide knowledge of the way in which certain impurities enter the lattice. For example, in GaAs cadmium and zinc are acceptor impurities known to replace gallium while sulfur and selenium are donor impurities known to replace arsenic.[1]

The measurements to be reported here plus the work of others indicate strongly that the basic mechanism of substitutional diffusion in these materials is one of atomic migration within one of the sublattices.[2–4]

---

* This work was supported by the Electronics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command.

[1] J. T. Edmond, Proc. Phys. Soc. (London) **73**, 622 (1959).

[2] L. Slifkin and C. T. Tomizuka, Phys. Rev. **97**, 836 (1955).

[3] F. Eisen and C. Birchenall, Acta Met. **5**, 265 (1957).

[4] B. Goldstein, *Properties of Elemental and Compound Semiconductors* (Interscience Publishers, Inc., New York, 1960), p. 155.

## II. EXPERIMENTAL RESULTS

### A. General Experimental Procedures

Single crystals of GaAs were grown by the magnetic Czochralski technique, and InP crystals were grown by the gradient freeze technique.[5] Details of the preparation of flat wafers of these materials, of the diffusion procedures, and of the determination of the penetration profiles have been given in earlier reports.[6,7] The wafers were all single crystal and strain-free as indicated by infrared birefringence examination. Dissociation of the InP and GaAs at the diffusion temperatures was prevented by the inclusion in the diffusion ampoules of appropriate amounts of phosphorus and arsenic, respectively.[8]

For those cases in which the diffusion proceeded from a thin electroplated layer the diffusion constants were obtained by fitting the penetration profile to the "fixed source" solution to the diffusion equation

$$C(x)=[Q/(\pi Dt)^{\frac{1}{2}}]\exp(-x^2/4Dt), \tag{1}$$

where $C(x)$ is the concentration, $Q$ is the amount of material initially deposited, $x$ is the penetration, $t$ is the time and $D$ is the diffusion constant. When the diffusion proceeded from a vapor source, the "constant source" solution was used,

$$C(x)=C_s\{1-\mathrm{erf}[x/2(Dt)^{\frac{1}{2}}]\}, \tag{2}$$

where $C_s$ is the initial concentration of diffusant in the crystal and the remaining terms are as defined for Eq. (1).[9]

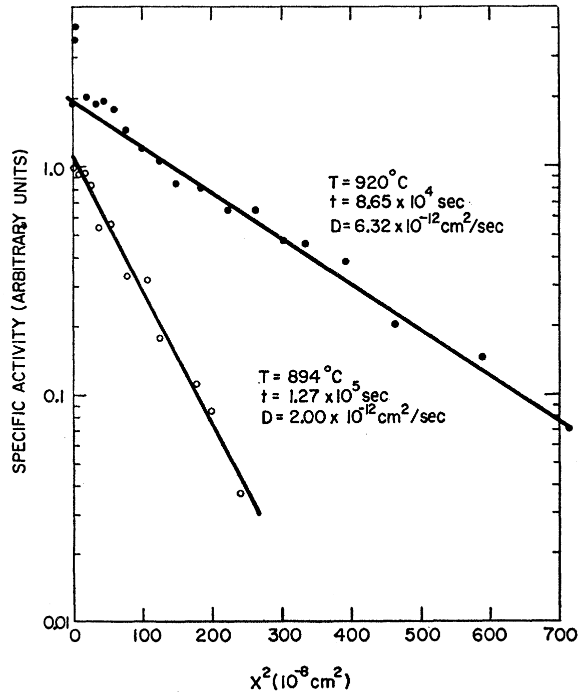


FIG. 1. Representative penetration profiles for the diffusion of In in InP from electroplated layers.

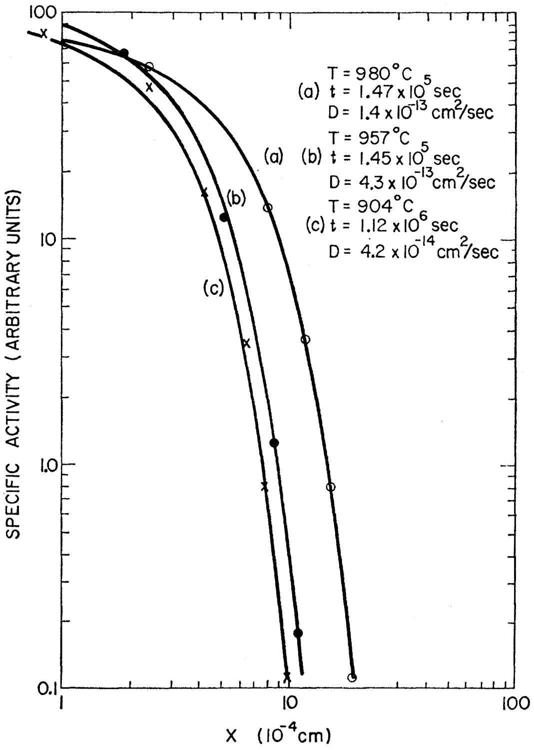


FIG. 2. Representative penetration profiles for the diffusion of P in InP from the vapor. Solid lines are the theoretical error function complement.

### B. Self-Diffusion in InP

For the indium diffusion the source was a thin electroplated layer of radioactive $In^{114}$ obtained from the Oak Ridge National Laboratory, while for the phosphorus diffusion the source was a vapor of radioactive red $P^{32}$ obtained from Atomic Energy, Canada. In the latter case an important step in the procedure was found to be the washing of the phosphorus in distilled water and anhydrous ether to eliminate $P_2O_5$ and the subsequent formation of $H_3PO_4$ which severely etched the InP at high temperatures.

Figures 1 and 2 contain representative penetration profiles for the indium and phosphorus diffusion, respectively. Penetrations of phosphorus were generally smaller than those of indium. This was due both to the smaller diffusion constants of phosphorus and also to

---

[5] L. Weisberg *et al.*, *Properties of Elemental and Compound Semiconductors* (Interscience Publishers, Inc., New York, 1960), p. 25.

[6] B. Goldstein, Rev. Sci. Instr. **28**, 289 (1957).

[7] B. Goldstein, Phys. Rev. **118**, 1024 (1960).

[8] J. Van den Boomgaard and K. Schol, Philips Research Repts. **12**, 127 (1957).

[9] A discussion of these solutions to the diffusion equation can be found in B. M. Barrer, *Diffusion in and Through Solids* (The Macmillan Company, New York, 1941).

the fact that phosphorus diffused from a vapor source while indium diffused from an electroplated metallic layer.[10] Plotting the diffusion constants against the reciprocal of the absolute temperature produces the curves shown in Fig. 3. Both curves can be described by the customary equation $D = D_0 \exp(-E/kT)$, where $D_0$ is $1\times10^5$ cm²/sec and $E = 3.85\mp0.05$ ev for indium, and $D_0$ is $7\times10^{10}$ cm²/sec and $E = 5.65\mp0.06$ ev for phosphorus.

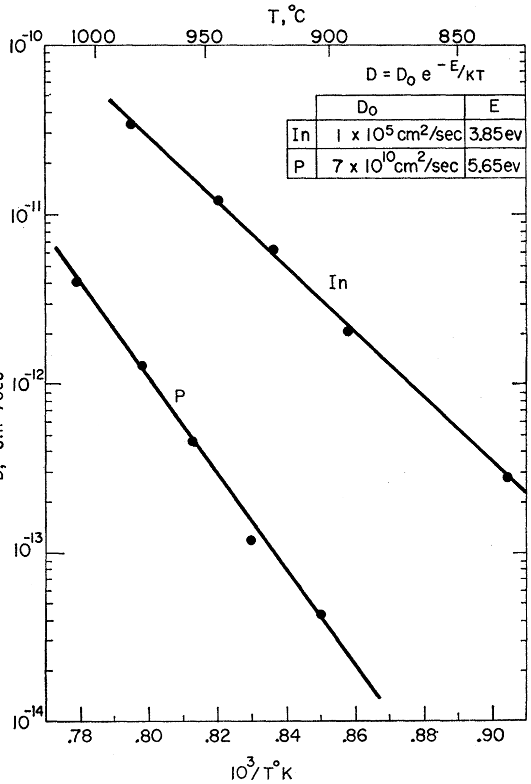


FIG. 3. Diffusion of In and P in InP.

## C. Self Diffusion in GaAs

Measurements of the diffusion of Ga and As in GaAs were severely hampered by very small diffusion penetrations and by the very short half-lives of the usable radio-isotopes which precluded long diffusion times. (The half-life of $Ga^{72}$ is 14 hours, that of $As^{76}$ is 27 hours.)[11] Nonetheless, good penetration profiles from electroplated layers of $Ga^{72}$ and from vapors of $As^{76}$ following the proper solutions to the diffusion equation were obtained. Figures 4 and 5 show such penetration profiles for gallium and arsenic diffusion, respectively, from which diffusion constants were calculated.

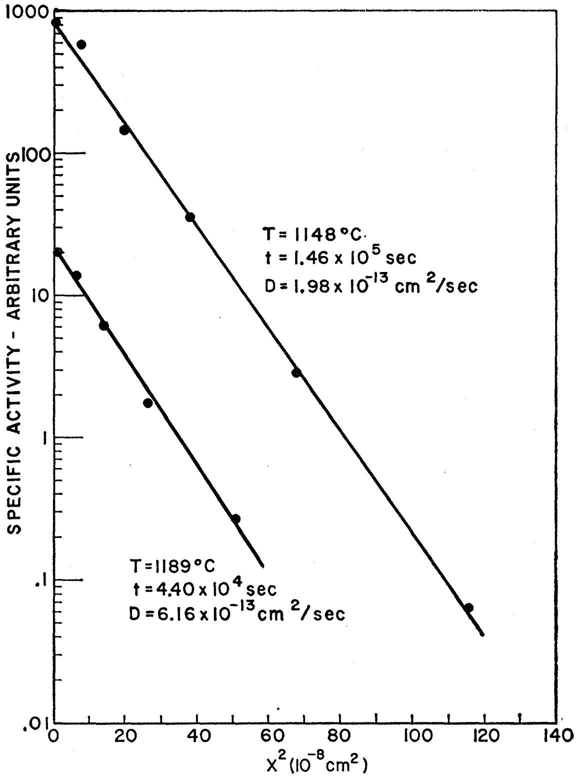


FIG. 4. Representative penetration profiles for the diffusion of Ga in GaAs from electroplated layers.

The temperature dependence of these diffusions is shown in Fig. 6. For gallium the customary behavior is found and the diffusion can be characterized by a $D_0$ of $1\times10^7$ cm²/sec and an activation energy $E$ of $5.60\mp0.32$ ev. For arsenic, however, a region of very low, relatively temperature-insensitive diffusion is observed before the expected Boltzmann-type behavior occurs at very high temperatures. The high-temperature region indicates an activation energy of $10.2\mp1.2$ ev. It is suggested that the relatively temperature-insensitive arsenic diffusion may be due to diffusion along dislocations or clusters of dislocations. Long, low-level tails in the diffusion profiles have very often been observed in these self-diffusion measurements which also suggest diffusion along dislocations.[12]

The most significant result of the self-diffusion measurements is the fact that in both InP and GaAs the constituent atoms diffuse at rates and with activation energies which are appreciably different.

## D. Diffusion of Cd and Zn in GaAs

This work was reported in detail in an earlier publication.[7] The diffusion of Cd and Zn in GaAs can be

---

[10] The phosphorus vapor consists chiefly of $P_4$ molecules, so that the initial entry of phosphorus atoms into the InP lattice may have been even further inhibited. Since the critical temperature of phosphorus is about 700°C, as much as 400 mg was used in a 10-cm³ ampoule in an attempt to increase the source concentration.

[11] These isotopes were supplied by the Industrial Reactor Laboratories, Plainsboro, New Jersey.

[12] G. P. Williams, Jr., and L. Slifkin, Phys. Rev. Letters 1, 516 (1958).

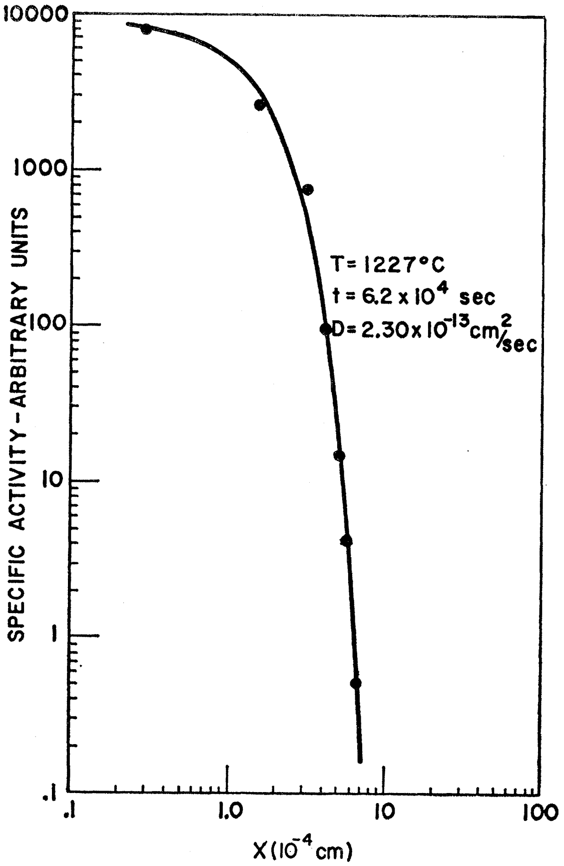


FIG. 5. Representative penetration profile for the diffusion of As in GaAs from the vapor. The solid line is the theoretical error function complement.

characterized, respectively, by a $D_0$ of 0.05 cm$^2$/sec and 15 cm$^2$/sec with activation energies $E$ of 2.43 ev and 2.49 ev, i.e., the same within experimental error.

### E. Diffusion of Sulfur and Selenium in GaAs

For the diffusion of sulfur, vapor sources as dilute as $3\times10^{16}$ [13]/cm$^3$ were found necessary to eliminate reactions at the surface of the GaAs. Figure 7 shows two representative penetration profiles obtained under these conditions. Initial sulfur concentrations in the GaAs for these curves are about $2\times10^{18}$/cm$^3$. The temperature dependence of the sulfur diffusion in the range from 1000°C to 1200°C is shown in Fig. 10. The data indicate a $D_0$ of $4\times10^3$ cm$^2$/sec and an activation energy of $4.04\mp0.15$ ev. When dense vapor sources of sulfur were used, $\sim10^{18}$/cm$^3$, the surfaces of the GaAs wafers showed evidence of a strong reaction with the sulfur. Electron diffraction patterns of these samples taken at grazing angle of incidence showed the presence of a GaS phase at the surface. Above a certain concentration ($\sim10^{20}$/cm$^3$) further additions of sulfur apparently produce GaS rather than increasingly doped GaAs. This emphasizes the distinction which should perhaps be made, especially when working with impurities and compound semiconductors, between the solubility of an impurity in which the host crystal retains its identity and miscibility of an impurity in which another phase may be formed.

When wafers of GaAs were heated in selenium vapor, an interesting side effect was observed, namely, the formation of layers at the surface which were clearly different from GaAs. These layers were amorphous, showed no sharp changes in optical absorption[14] in the visible or near infrared, and varied in thickness with selenium vapor density. The recent work of Flaschen *et al.*[15] on selenium glasses, plus the characteristics described above strongly suggest that the most likely explanation of this effect is that a selenium glass has formed on the GaAs surface. In Fig. 8 is shown a photograph of a cross-sectioned wafer of GaAs heated at 1008°C in selenium vapor of density $6\times10^{18}$/cm$^3$. Directly beneath the photograph is a plot of selenium radioactivity vs penetration for this wafer. The extent of the flat region corresponds roughly to the depth of the surface layer from which the diffusion of selenium into GaAs apparently has proceeded. When diffusion

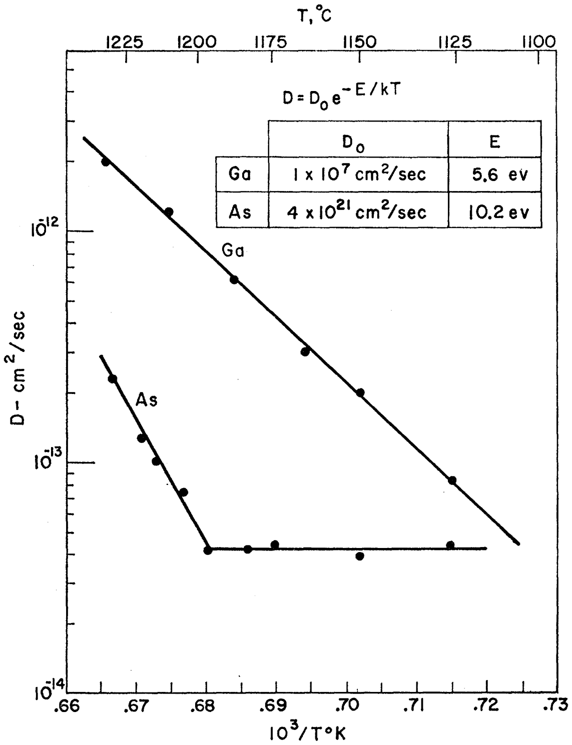


FIG. 6. Diffusion of Ga and As in GaAs.

---

[13] The vapor densities given for the sulfur and selenium work are atomic densities and do not take into account the fact that both sulfur and selenium vapor are molecular, each molecule containing from 2 to 8 atoms.

[14] Optical measurements were kindly performed by W. Spicer of these Laboratories.

[15] S. S. Flaschen *et al.*, J. Am. Ceram. Soc. 42, 450 (1959).

anneals were run with lower vapor source densities, $\sim 5\times 10^{17}/\text{cm}^3$, initial flat regions in the penetration profiles were still found but they were very shallow, of the order of several microns. Furthermore, if the penetration curves are replotted using the end of the initial flat region as the "zero" for the remainder of the curve, then it is found that the resulting curves follow the error function complement quite well. (This is, of course, what one would expect if a source layer of appreciable thickness did form at the surface.) This procedure is illustrated in Fig. 9 for an anneal at 1105°C, showing both the raw data and the reduced curve. The initial selenium concentrations in the GaAs for these diffusion anneals vary between 1 and $2\times 10^{21}/\text{cm}^3$. The temperature dependence of the diffusion of selenium in GaAs, calculated as described above, is shown in Fig. 10 together with the sulfur diffusion results. It is characterized by a $D_0$ of $3\times 10^3$ cm²/sec and an activation energy of $4.16\mp 0.15$ ev, i.e., the same within experimental error as that for sulfur.

### F. Precision of the Measurements

Details of the precision of the experimental procedures are essentially the same as those given in an earlier report.[7] Estimates of the uncertainty in *D*, both from using median penetration distances and from graphically using the error bounds of each data point, are in the region $\mp 10\%$ to $\mp 15\%$. Uncertainties in *E* are derived from a least squares straight line of $\ln D$ vs $1/T$. Deviations of measured values of *D* from this straight line also fall within $\mp 15\%$.

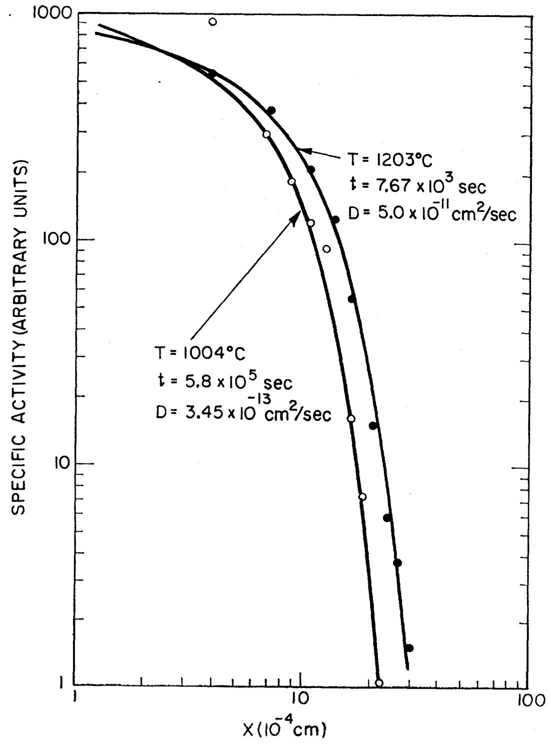
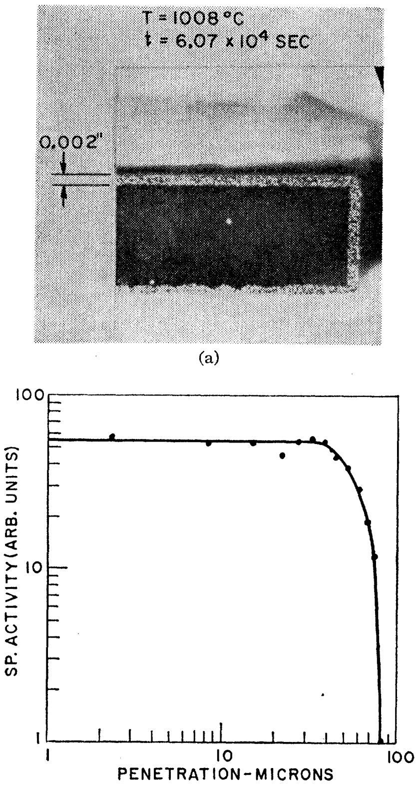


FIG. 7. Representative penetration profiles for the diffusion of S in GaAs from the vapor.



(a)

(b)

FIG. 8. Photograph of the edge of a cross-sectioned GaAs wafer heated in Se vapor at a temperature of 1008°C for $6.07\times 10^4$ sec, showing a glassy layer of Se which has formed at the surface. Directly beneath it is the penetration profile of the radioactive Se for this wafer.

### III. DISCUSSION

The large disparity in diffusion constants and activation energies for InP and GaAs speaks against a mechanism of diffusion involving atomic migration via nearest neighbor vacancies or via a ring mechanism involving equal numbers of atoms of each species. Each Column III atom has for its nearest neighbors four Column V atoms (or vacancies) and vice versa. Hence, a substitutional diffusion mechanism involving nearest-neighbor vacancy interchange should result in very nearly equal diffusion coefficients and activation energies for both species of atoms. Since interstitial diffusion would appear to be ruled out by the very low diffusion constants and high activation energies, the data presented here suggests that the likeliest mechanism of diffusion is the migration of each atomic species through its own sublattice. This mechanism has been suggested as a possibility for self-diffusion in ordered alloys in general,[2] and in particular as the mechanism for self-diffusion in InSb and GaSb.[3]

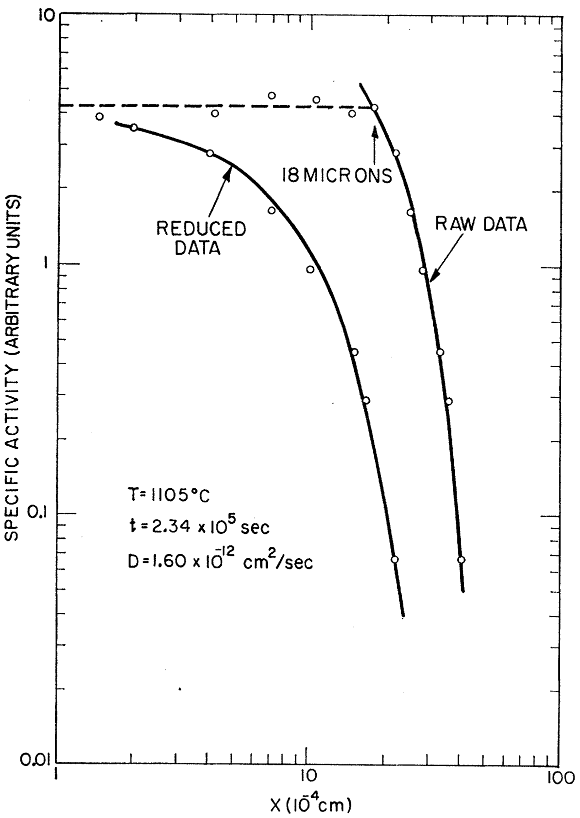


FIG. 9. Penetration profile for the diffusion of Se in GaAe, showing how subtracting the end of the initial flat region from the remainder of the "raw data" curve produces the complsmentary error function.

Recently, it was suggested that the concept of self-diffusion proceeding within a specific sublattice be extended to include impurity diffusion when the impurity is incorporated into the crystal as a substitutional donor or acceptor.[4] The data in Table I, a summary of the important self- and impurity-diffusion behavior in GaAs, strongly support this suggestion. Cd and Zn, which enter the Ga sublattice, diffuse with the same activation energy, about 2.5 ev, and S and Se, which enter the As sublattice, diffuse with the same activation energy, about 4.1 ev. Based on our knowledge of substitutional donor and acceptor diffusion in the elemental semiconductors germanium and silicon,[16] this behavior is what one might expect if Cd and Zn diffused through the Ga sublattice, and S and Se through the As sublattice. Note in Table I that among the donors and acceptors the larger atom diffuses more slowly.

Other work on impurity diffusion in compound semiconductors tends to substantiate further the idea of diffusion within a sublattice. Measurements of *p-n* junction migration in InAs[17] show that all atoms substituting in the Column III sublattice, whether they be Column II acceptors or Column IV donors, diffuse with the same activation energy, and all Column VI donors (excepting tellurium whose results are ambiguous[17]) diffuse with the same activation energy: however, these energies are different, 1.2 ev for atoms occupying Column III lattice sites and 2.2 ev for atoms occupying Column V lattice sites.

The InP self-diffusion results described earlier indicate that size, *per se*, does not seem to be a dominant factor in the diffusion. The covalent tetrahedral radius of indium is 1.44 A while that of phosphorus is only 1.10 A.[18] Yet phosphorus diffuses more slowly than indium and with a higher activation energy. An indication of what the dominant factor might be can be derived from the observation that in all the available diffusion data for compound semiconductors the Column V sublattice diffusion is characterized without exception by higher activation energies than that of the corresponding Column III sublattice diffusion, as seen, for example, in Table I. This observation supports the suggestion[3] that if the diffusing atoms are neutral (or singly ionized for the substitutional impurities) then the motion of a Column V vacancy may require more energy than the motion of a Column III vacancy, since the former involves the removal of five electrons from the bond system, while the latter involves the removal of only three electrons.

In conclusion it is to be noted that the activation energies and $D_0$ values reported here for self-diffusion are among the highest to be found in the literature. However, based on self-diffusion measurements in germanium, there may be some reason to expect this, as follows.

Consider first the high activation energies. Germanium melts at 936°C and has a band gap of 0.7 ev. Indium phosphide melts at 1070°C and has a band gap of 1.25 ev, indicating that its bond energies are higher than that of germanium. This, plus the fact that in InP the basic diffusion jump is not to a nearest neighbor lattice site (as it is in germanium) but to a second-nearest neighbor site, makes it not unreasonable that activation energies for self-diffusion in InP are 3.85 ev

TABLE I. Diffusion in gallium arsenide.

| | $E$, ev | $D_0$, cm$^2$/sec | $D_{1100°C}$ | | $E$, ev | $D_0$, cm$^2$/sec | $D_{1100°C}$ |
|---|---|---|---|---|---|---|---|
| Zn | 2.49 | 15 | $1.5\times10^{-8}$ | S | 4.04 | $4\times10^{3}$ | $6.0\times10^{-12}$ |
| Cd | 2.43 | 0.05 | $1.0\times10^{-12}$ | Se | 4.16 | $3\times10^{3}$ | $1.6\times10^{-12}$ |
| Ga | 5.60 | $1\times10^{7}$ | $3.5\times10^{-14}$ | As | 10.2 | $4\times10^{21}$ | $1.0\times10^{-16}$ (extrapolated) |

---

[16] The crystal structure of germanium and silicon is identical to that of the III–V compound semiconductors. In germanium all donors and acceptors diffuse with the same activation energy [W. C. Dunlap, Phys. Rev. **94**, 1531 (1954)] and in silicon they differ only very little [C. Fuller *et al.*, J. Appl. Phys. **27**, 544 (1957)].

[17] A. Schillman, Z. Naturforsch. **11a**, 472 (1956).

[18] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939).

and 5.65 ev compared to 3.0 ev for germanium. Similarly, even higher activation energies for GaAs, which melts at 1240°C and has a band gap of 1.40 ev, are only to be expected.

Next, consider the $D_0$ values. Following Zener,[19] we write for $D_0$ the expression

$$D_0=\gamma a^2 \nu \exp(\Delta S/R), \tag{3}$$

where $\gamma$ is a numerical factor of the order 0.1 to 1 determined by the geometry of the diffusion jump, $a$ is the lattice constant of the host crystal, $\nu$ is a vibrational frequency, and $\Delta S$ is the total activation entropy. Since order-of-magnitude changes in the pre-exponential part of Eq. (3) are highly unlikely in comparing, for example, germanium to InP, the unusually large $D_0$'s reported here must reflect a larger $\Delta S$. For germanium $\Delta S$ calculated from the measured $D_0$ is 16 cal/mole-deg. Both Zener's theory and an empirical relationship evolved by Dienes[20] contain the result that $\Delta S$ varies as $E$, the activation energy. If this is applied to the self-diffusion data of InP, activation entropies of 21 and 30 cal/mole-deg are predicted. When the $D_0$'s reported in the present work are used, together with the appropriate constants in Eq. (3),[21] activation entropies of 30 and 56 cal/mole-deg are calculated. Since it is presumed that the basic diffusion step in the compound semiconductors is the movement of an atom to a second-nearest neighbor site rather than to a nearest neighbor site, the activation entropy for the former process may be intrinsically higher than that of the latter process. This would add, then, to the entropy values extrapolated from the germanium work and bring them qualitatively closer to the values calculated from the $D_0$'s in the present work. In the case of self-diffusion in GaAs, even with a $D_0$ of $10^{21}$ cm$^2$/sec for arsenic diffusion, the activation entropies are less than a factor of two greater than those extrapolated from the germanium data. It is to be strongly emphasized that these considerations are not meant to indicate either a quantitative agreement with other work, or an understanding of the physical significance of large activation entropies. Rather, it is suggested that these considerations indicate that the unusually large $D_0$'s reported here may not be so unreasonable.

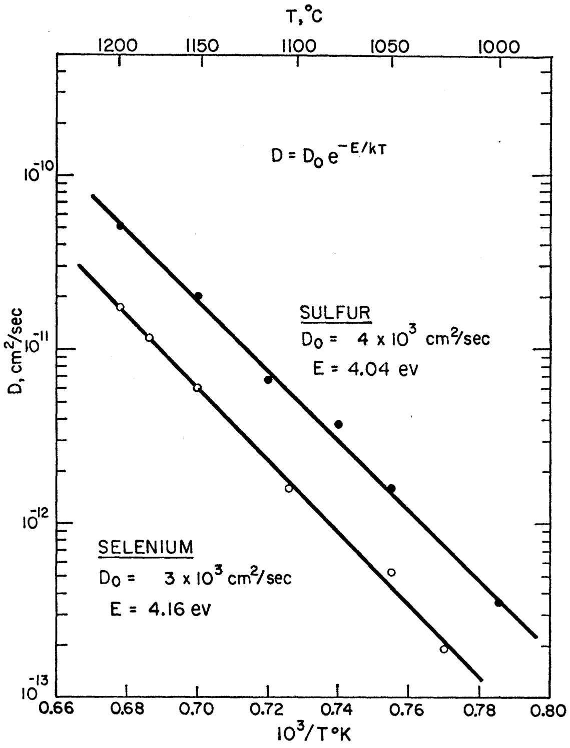


FIG. 10. Diffusion of S and Se in GaAs.

## ACKNOWLEDGMENTS

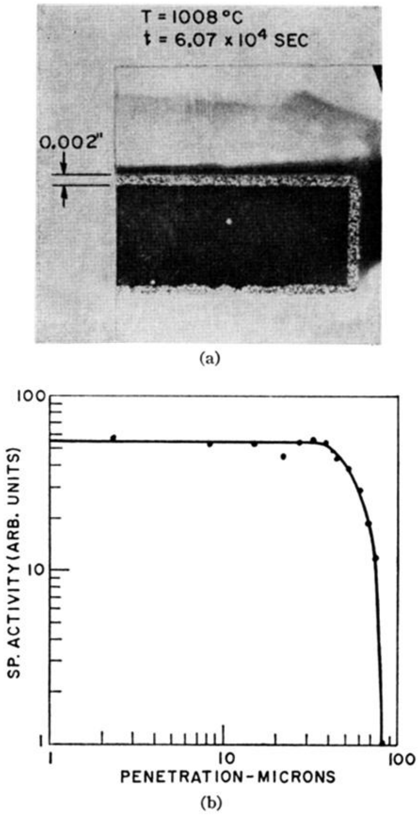
The author is very pleased to acknowledge the many interesting and helpful discussions he has had with many of his colleagues during the course of this work. He would like to thank P. Herkart and J. Blanc for supplying the single-crystal GaAs, and B. Seabury and R. Guire for supplying the single-crystal InP. Finally, he would like to express his thanks to Mrs. C. Dobin for her technical assistance in this work.

---

[19] C. Zener, J. Appl. Phys. **22**, 372 (1951).

[20] G. J. Dienes, J. Appl. Phys. **21**, 1189 (1950).

[21] For diffusion within a face-centered cubic sublattice of these materials $\gamma$ is 1. The lattice constants for InP and GaAs are 5.87 A and 5.64 A, respectively. For $\nu$, we have taken the longitudinal lattice vibrational frequencies reported by G. Picus *et al.*, J. Phys. Chem. Solids **8**, 282 (1959).



(a)

(b)

FIG. 8. Photograph of the edge of a cross-sectioned GaAs wafer heated in Se vapor at a temperature of 1008°C for $6.07 \times 10^4$ sec, showing a glassy layer of Se which has formed at the surface. Directly beneath it is the penetration profile of the radioactive Se for this wafer.