Table I. Lifetime in the $N$-type Ge in which resistivity is 32 ohm-cm and mobility is 1700 $cm^2$/v-sec.

| Lifetime ($\mu$sec) | Mean life path (mm) | $E$(v/cm) |
|---|---|---|
| 27 | 1.5 | 3.3 |
| 26 | 1.1 | 2.5 |

For instance, in the curve $N$ the thermal noise power with the light and the field absent is 27 $\mu$a in the current of the square law detector, with the field present and the light absent 67 $\mu$a, and with the light and the field present is indicated by circles on the solid line. The noise power with the field only present is larger than the noise power with the field and the light both present at the right edge of the left terminal, in which the minority carriers enter. But these do not arrive at the right terminal without the direction of the field changing. Each dc current through the filament with the light and the field both present is indicated by dotted lines $I$ and $I'$. In this case each dc current increased by light (whose luminous intensity is about 0.028 lumen) is 90 $\mu$a and 60 $\mu$a, respectively. From these curves the lifetime of the injected minority carriers is calculated according to the Eq. (1) and tabulated in Table I.

The frequency dependence of the noise by the narrow band measurements should exhibit an oscillatory behavior as in the results obtained by Hill and Van Vliet.[2] But the noise spectrum illuminated by light at the midpoint of the filament does not change in shape between the frequencies from 3 kc/sec to $10^4$ kc/sec, while our measurements were made in steps of the large frequencies. When the length of the illuminated region varies, the noise power increases about proportional to the length. But the life path seems not to vary.

PHYSICAL REVIEW VOLUME 118, NUMBER 4 MAY 15, 1960

# Diffusion of Cadmium and Zinc in Gallium Arsenide†

B. Goldstein
*Radio Corporation of America Laboratories, Princeton, New Jersey*
(Received December 4, 1959)

The diffusion of Cd and Zn in GaAs has been studied by using radioactive isotopes of these elements as tracers. The diffusion of Cd follows the correct solution to the diffusion equation and its temperature dependence is of the customary form, $D=D_0 \exp(-E/kT)$ where $E$, the activation energy, is 2.43 ev and $D_0$ is 0.05 $cm^2$/sec. The diffusion of Zn from the vapor cannot, however, be described in terms of a single diffusion constant. The penetration curves decrease much more sharply than they theoretically should. Hall measurements indicate that all the Zn is substitutional and that it forms an impurity conduction band merging with the valence band. When Zn diffuses from a thin electroplated layer of radio-zinc, then the penetration profiles do correspond to the proper solution to the diffusion equation. The diffusion constants so determined have the usual temperature dependence given by $D=D_0 \exp(-E/kT)$, where $D_0$ is 15 $cm^2$/sec and $E$ is the same as that found for Cd. From the work reported here and that of others, it is suggested that the diffusion of Cd and Zn in GaAs proceeds via vacancy migration within the gallium sublattice.

## I. INTRODUCTION

In the course of a study of diffusion in compound semiconductors composed of elements from columns III and V of the periodic table, the diffusion of cadmium and zinc was studied in gallium arsenide. These elements have been found to be acceptors in GaAs,[1] and are presumed to enter the lattice substitutionally, replacing gallium atoms. The purpose of this work was to measure the important parameters of the diffusion, such as the diffusion coefficient and the activation energy, and also to determine as much as possible about the specific mechanism of the diffusion.

† 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).

## II. EXPERIMENTAL PROCEDURES AND RESULTS

### A. Diffusion of Cadmium

The general experimental procedure was as follows: Single crystal wafers of GaAs, $\frac{3}{16}$ in. square and about 50 mils thick were cut, lapped flat to within 0.1 micron across their surfaces, and then polished to a mirror finish. The wafers were then placed on quartz flats and heated in evacuated quartz ampoules for appropriate times at temperatures ranging from 868°C to 1149°C in regulated furnaces. Pieces of pure Cd, which had been sent to the Oak Ridge National Laboratory for irradiation, producing radioactive $Cd^{115}$ (43-day half-life), were included in the ampoule to produce the vapor source for the diffusion. An amount of arsenic was also included to produce a pressure sufficient to prevent dis-

sociation of GaAs at the diffusion temperature.[2] Cooling was carried out with a cold zone at one end of the ampoule to avoid condensation of metallic Cd on the GaAs wafers. After cooling, the edges of the wafers were ground off to a depth many times the Cd penetration. Planar sections, perpendicular to the direction of the diffusion, were then removed using a precision lapping device,[3] and the penetration profile was obtained by measuring the specific activity in each lapped section with standard end-window Geiger counting techniques.

Upon cooling from temperatures of about 1000°C and over, however, the surface of the GaAs wafers was seen to swell and "blister," making it unusable for sectioning. Results obtained after introducing variations in the annealing and cooling procedures and using different amounts of Cd suggest that this was due to the rapid escape of Cd from the surface of the GaAs when the Cd pressure over the GaAs was suddenly removed by the application of the cold zone.[4] This difficulty was overcome by covering the wafer with a quartz flat and including in the ampoule two uncovered "dummy" wafers of GaAs. In this case it was found that while the "dummy" wafers blistered, the covered wafer did not.

In Fig. 1 are shown three representative diffusion penetration profiles. Penetrations varied from about 0.75 mil at 868°C to about 2.5 mils at 1149°C. The data

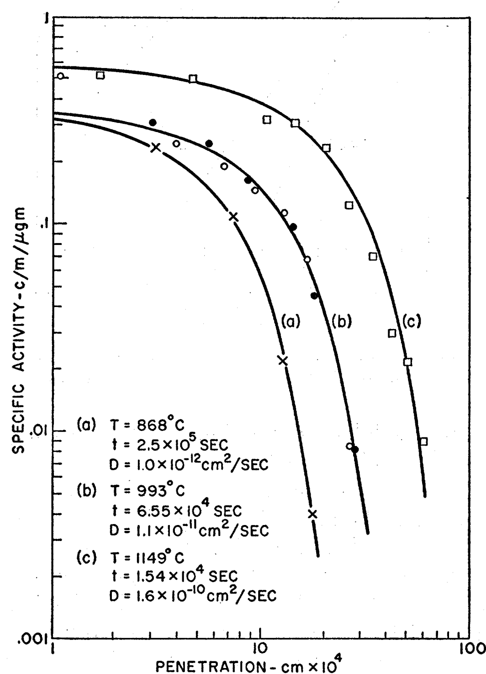


FIG. 1. The diffusion of cadmium in gallium arsenide. The solid lines are the theoretical error function complements.

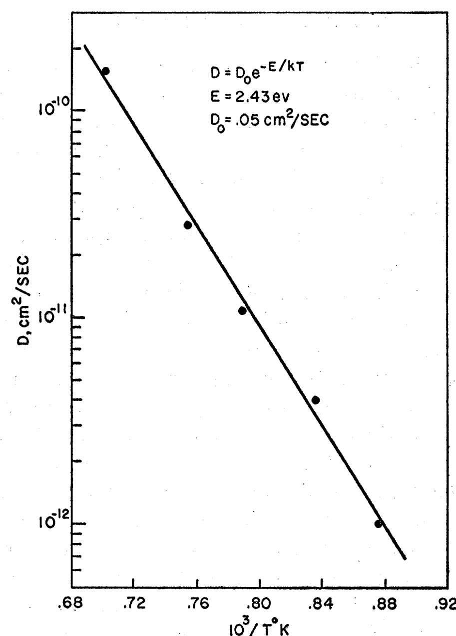


FIG. 2. The diffusion of cadmium in gallium arsenide.

can be described well by the complementary error function (solid lines in Fig. 1),

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

which is the solution to the diffusion equation for the "constant source" boundary condition.[5] The two sets of data for the 993°C curve correspond to diffusion across both a polished face and an unpolished (but lapped) face of the same wafer. Apparently polishing has a negligible effect on the shape and extent of the diffusion profile at these penetrations. The diffusion constants, $D$, in cm²/sec were obtained by fitting the data at each temperature to Eq. (1), where $C_s$ is the source concentration (in the solid), $x$ is the penetration in cm, $t$ is the time in seconds, and $T$ is the temperature.

In Fig. 2 is plotted the temperature dependence of the diffusion constants shown in Fig. 1. The behavior follows the customary equation, $D=D_0e^{-E/kT}$. The activation energy calculated from this curve is $E=2.43 \pm 0.06$ ev, and $D_0=0.05$ ($\pm 0.04$) cm²/sec.

By using absolute counting procedures, actual Cd concentrations were obtained. It was found that both the Cd vapor densities[6] and the initial Cd concentrations in the GaAs varied between 2 and $5\times10^{19}$/cm³. Thus, this figure represents a lower limit to the solid solubility of Cd in GaAs.

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

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

[4] Apparently, below about 1000°C the pressure of Cd in GaAs was not sufficient to cause the "blistering."

[5] A discussion of this and other solutions to the diffusion equation can be found by R. M. Barrer, in *Diffusion in and Through Solids* (The Macmillan Company, New York City, 1941).

[6] At lower temperatures, this corresponds to the saturated vapor pressure of Cd. At the higher temperatures, the density was kept low to help avoid the "blistering" described earlier.

## B. Diffusion of Zinc in GaAs

While the diffusion of Cd into GaAs from the vapor apparently behaves as expected, it was found that the penetration of Zn into GaAs from the vapor in the temperature range 800°C–1000°C can *not*, in general, be analyzed in terms of a single diffusion constant. Although the initial regions of the penetration profiles seem to follow an error function complement, in the deeper regions the data fall sharply below this curve, thus confirming a behavior initially reported by Allen and Cunnell.[7] After studying this diffusion as functions of temperature, time and vapor source density, three principal features became apparent. First, very large changes (greater than 10 times) in $C_{vap}$, the vapor source density, produce correspondingly very small changes (less than two) in $C_s$, the initial or surface concentration in the GaAs. Secondly, for the same time and temperature of diffusion, large changes in $C_{vap}$, although producing relatively little change in $C_s$, produce very large changes in both the extent and shape of the penetration. Finally, a small $C_{vap}$ ($\sim 10^{17}/cm^3$) produces a large $C_s$ ($\sim 10^{20}/cm^3$). These characteristics are illustrated in Fig. 3. Here it can be seen that even though $C_{vap}$ differs by more than an order of magnitude, $C_s$ changes only very little; and even though $C_s$ changes very little, there is a large change in the penetration. For very small $C_{vap}$ the penetrations apparently can be described by the error function complement but the diffusion constants obtained from these curves remain uncertain because the penetration still varies with $C_{vap}$.

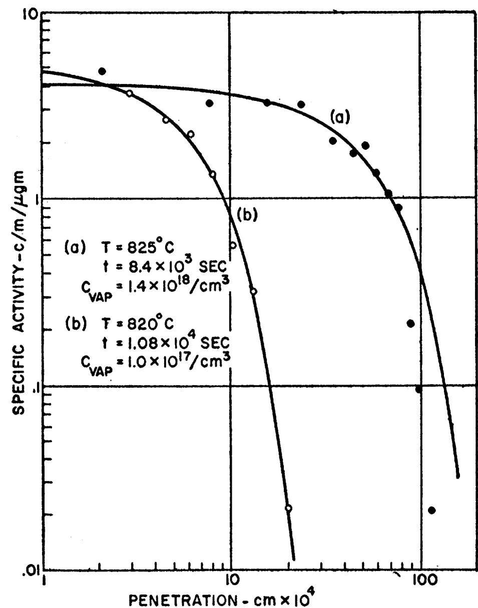


FIG. 3. Penetration profiles for the diffusion of zinc in gallium arsenide from the vapor. Note that a large change in $C_{vap}$ produces only a small change in $C_s$ but a large change in the penetration.

A firm explanation for the anomalous behavior of Zn described above cannot be offered at this time. Hall measurements[8] on GaAs wafers diffused to saturation with Zn show that there are indeed $10^{20}/cm^3$ free holes present, indicating that the Zn occupies substitutional sites. Lack of deionization down to liquid helium temperatures indicate further that Zn in these concentrations forms an impurity band merging with the valence band. These data appear to rule out the possibilities that the behavior is caused by the presence and diffusion of both ionized and unionized Zn at different rates, as proposed by Allen and Cunnell,[7] or by the presence and diffusion of interstitial and substitutional Zn at different rates. As a possibility, it is suggested that at these high Zn concentrations, the anomalous diffusion may be related to a solid-state reaction in which a compound such as $Zn_3 As_2$ is formed.

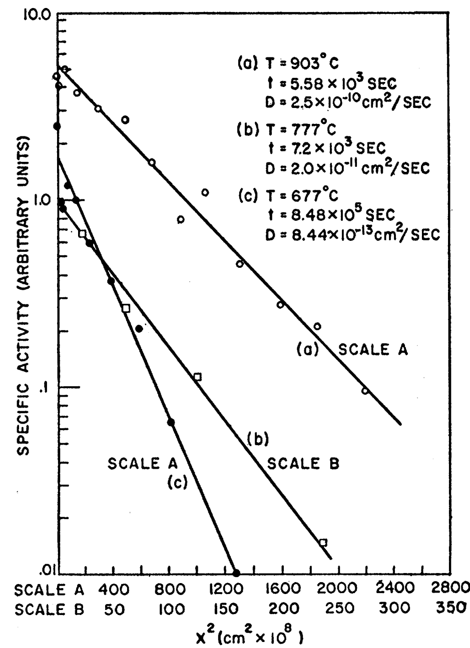


FIG. 4. Penetration profiles for the diffusion of zinc in gallium arsenide from an electroplated surface layer of radio-zinc.

In an attempt to produce a situation in which the diffusion might be more simple, studies were continued at temperatures below 800°C. Because of the low Zn vapor density at these temperatures, the diffusion source was an electroplated layer of radio-zinc less than 1 micron thick. The penetration profiles resulting from these diffusion anneals were found to follow the solution to the diffusion equation corresponding to the "fixed source" boundary condition,

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

where $Q$ is the amount of material initially deposited

[7] J. Allen and F. Cunnell, Nature **182**, 1158 (1958).

[8] Kindly performed by D. Meyerhofer of these laboratories.

(electroplated in this case) and the rest of the symbols are as given for Eq. (1). Figure 4 shows some typical curves, at the temperatures and for the times given, from whose slopes were calculated the values of $D$. The temperature dependence of these diffusion constants is plotted in Fig. 5. When the data from the only successful diffusion runs with electroplated layers[9] at temperatures above 800°C are added to the data taken below 800°C, all the data can be described by the usual equation $D=D_0e^{-E/kT}$. Here $E$ the activation energy is $2.49\pm0.05$ ev and $D_0$ is 15 ($\pm7$) cm²/sec.

### C. Precision of the Measurements

Errors in specific activity varied from $\pm4\%$ to $\pm10\%$ depending on counting rate. Errors in the penetration totaled $\pm6\%$. The total error in $D$, however, is difficult to calculate in an analytical manner since both the ordinate and the abscissa of the penetration curves are measured quantities containing errors. If median values for $x$, the penetration distance, are used then the error in $D$ can be estimated to be about $\pm15\%$. The error in $D$ has also been estimated graphically by drawing the penetration curves through the actual error bounds of each data point: This procedure results in an uncertainty in $D$ of $\pm10\%$ to $\pm15\%$. The uncertainty in $E$ was calculated from a least squares straight line of ln $D$ vs $1/T$ and is about $\pm3\%$. The concomitant uncertainty in $D_0$ is $\sim50\%$ to 100%.

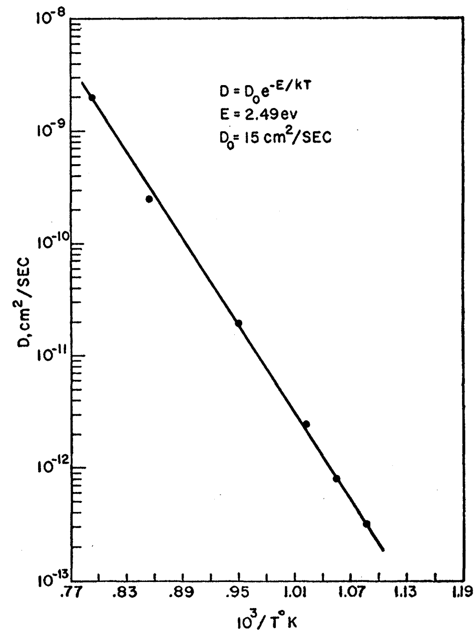


FIG. 5. The diffusion of zinc in gallium arsenide from electroplated surface layers.

## 3. DISCUSSION

The fact that the activation energies for the diffusion of Zn and Cd are the same would indicate that the dominant Zn diffusion process apparently isolated at the lower temperatures (<800°C) is the same as that governing the Cd diffusion. It is, of course, not surprising to find that substitutional atoms, in this case acceptors, should have the same activation energy if they diffuse by vacancy migration. For example, in germanium all substitutional impurities diffuse with essentially the same activation energy,[10] in silicon they differ only little,[11] and in InAs acceptors have been found to diffuse with the same activation energy.[12]

In studies of self-diffusion in InSb and GaSb, Eisen and Birchenall have found that the diffusion constants and activation energies for the column III elements and column V elements are different.[13] From this it was concluded that the likeliest mechanism for this diffusion is vacancy migration within a specific sublattice of these materials.[14] Slifkin and Tomizuka have also presented this suggestion.[15] In addition, it has recently been found that in InP, the diffusion of indium and phosphorus proceeds at different rates and with different activation energies[16] (3.85 ev for indium and 5.65 ev for phosphorus). It is suggested here that the concept of self-diffusion proceeding within one of the sublattices be extended to include substitutional impurity diffusion which takes place via vacancy migration. In the work described here, this would mean that Cd and Zn diffuse through the Ga sublattice in GaAs. This proposal tends to be substantiated by work on InAs[12] in which it is found that while acceptors diffuse with the same activation energy, and donors (with the exception of tellurium) diffuse with the same activation energy, these energies are different, being 1.2 ev for the former and 2.2 ev for the latter. Further work on the diffusion of the donors sulfur and selenium in GaAs is currently under way and should shed more light on this question.


### ACKNOWLEDGMENT

The author wishes to thank Dr. J. Blanc for supplying the single crystal GaAs, and Mrs. C. Dobin for her technical assistance during the course of this work.


[9] By this is meant those diffusion anneals which produced penetration profiles corresponding to a proper solution of the diffusion equation. The difficulty with electroplated layers at temperatures over 800°C was that apparently most of the Zn plate evaporated before entering the GaAs lattice.

[10] W. C. Dunlap, Phys. Rev. **94**, 1531 (1954).

[11] C. Fuller, et al., J. Appl. Phys. **27**, 544 (1957).

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

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

[14] The structure of these compound semiconductors is of the diamond type, consisting of two interpenetrating face-centered cubic sublattices, each sublattice being made up of one of the constituent elements.

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

[16] B. Goldstein (unpublished).

*Note added in proof.*—Results recently obtained on the diffusion of sulfur and selenium in GaAs indicate an activation energy for both of about 4.0 ev, consistent with the concept of sublattice impurity diffusion discussed above.