(2) The  $Z_1$  center cannot arise from the capture of an electron by an I.V. dipole followed by a dissociation

$$(Sr^{++}\oplus)+e^- \rightarrow Z_1+\oplus$$

according to one of the mechanisms suggested by Seitz. The absence of dichroism<sup>11</sup> and E.P.R. (electron paramagnetic resonance)<sup>12,13</sup> measurements support the picture of a center having a spherical symmetry, as the Seitz one does. On the other hand hyperfine structure of  $Z_1$  center in KCl:SrCl<sub>2</sub>, enriched in the magnetic isotope Sr<sup>87</sup>, has not been pointed out by the latest ENDOR<sup>14</sup> (electron nuclear double resonance) measurements, as expected on the basis of the Seitz model. The energy absorbed by the electron in the transition from the ground state to the first excited state has been calculated by several authors on the basis of the Seitz model, and the results are very far from the experimental value of 2.06 eV in KCl:SrCl<sub>2</sub> at L.N.T.

<sup>11</sup> N. Ishiguro, E. Sugioka, and N. Takeuchi, J. Phys. Soc. Japan 15, 1302 (1960). <sup>12</sup> G. E. Conklin and R. J. Friauf, Phys. Rev. 132, 189 (1963). <sup>13</sup> H. Kawamura and R. Ishiwatari, J. Phys. Soc. Japan 13, 754 (4075).

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Lidiard<sup>5</sup> by means of thermodynamic arguments calculates an energy of 0.9 eV which would localize the  $Z_1$ band in the infrared. Johnson and Scott,<sup>6</sup> by following the scheme of Simpson for the F center, obtain an energy of about 9 eV; a better agreement with the experimental measurements is encountered in calculations of Peterson and Patterson,<sup>7</sup> who found an energy of 3.14 and 2.59 eV, respectively, for the Seitz and Pick models.

Since Bushnell's measurements rule out the Seitz model, the  $Z_1$  growth might be due to an ionic process, as with the one proposed by Lüty: an empty anion vacancy, resulting from the *F*-center optical ionization, diffuses in the lattice until it is captured close to an impurity. If this mechanism holds, however, our experimental results suggest that the impurity is an isolated divalent metal impurity not an I.V. complex.

### ACKNOWLEDGMENTS

The authors are indebted to Professor R. Fieschi for extensive and helpful discussions of this topic and to Dr. S. Fornili and Dr. G. Rossi for considerable help in performing the measurements.

PHYSICAL REVIEW

VOLUME 143, NUMBER 2

**MARCH 1966** 

# Self-Diffusion in Silicon Carbide\*

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In available crystals, the self-diffusivity of carbon has been found to be extrinsic (experimental range 1853 to 2088 °C), the carbon self-diffusivity being higher in p-type than in n-type material. The self-diffusion coefficient for Si is approximately ten times higher than that for carbon between 1927 and 2017 °C.

# I. INTRODUCTION

**HE** influence of changing chemical-bond type on the disorder type, the point-defect concentration, the defect mobilities, and hence atom diffusivities in compounds, is incompletely understood. In the transition from ionic to covalently bonded materials, the criterion for maintaining electroneutrality shifts from ion vacancy to electron or hole generation to compensate for a valence difference between the host and an added impurity. This sometimes leads to different effects on self-diffusivities; in a covalent compound the defects on the respective sites may form with electron or hole compensation rather than being connected by a

Schottky equilibrium. It would appear that substitutional disorder would be more important in governing self-diffusivities in covalent compounds. Such detail has not been elucidated among the Group IV semiconductors<sup>1,2</sup>; in germanium<sup>3,4</sup> the self-diffusivity has been measured, while in silicon<sup>5-7</sup> it has only been inferred. However, impurity diffusion in Ge and Si has been rather well documented. We report here data for some p-type and n-type SiC crystals and on p-type

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<sup>&</sup>lt;sup>1</sup> J. R. O'Connor and J. Smiltens, Silicon Carbide: A High Temperature Semiconductor (Pergamon Press, New York, 1960). <sup>2</sup> R. A. Swalin, J. Appl. Phys. 29, 670 (1958). <sup>8</sup> H. J. Letaw, W. M. Portnoy, and L. Slifkin, Phys. Rev. 102, 636 (1956); 93, 892 (1954). <sup>4</sup> M. W. Valenta and C. Ramasastry, Phys. Rev. 106, 73 (1957).

<sup>&</sup>lt;sup>5</sup>C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. 27, 544 (1956).

<sup>&</sup>lt;sup>6</sup> C. Elbaum, Phil. Mag. 5, 669 (1960).

<sup>&</sup>lt;sup>7</sup> M. S. Saidov, Elektronno-Dyrochnye Perekhody v Poluprov., Akad. Nauk SSSR, Akad. Nauk Uz. SSR, Tashkentsk. Gos. Univ. 1962, 275 (1962).

polycrystalline silicon carbide, to contribute to the basis for understanding self-diffusivities in covalent materials.

Initial experiments were performed to determine the slower diffusing species in SiC self-diffusion. Then the slower diffusing species was studied in greater detail as a function of temperature and impurity type. The impurity type and level were, however, limited by the availability of material. This work also evaluated a new technique<sup>8</sup> in the determination of silicon diffusion coefficients in SiC.

# **II. EXPERIMENTAL**

Silicon carbide crystals (6H) were procured from the Norton Company, Worcester, Massachusetts and from Dr. R. Hornstra, Philips Research Laboratories, Eindhoven, The Netherlands. A representative sample of the batch of crystals was analyzed chemically and spectrochemically. The black crystals were p-type governed by about 600 ppm Al impurity. The green crystals were *n*-type due to about 100 ppm N impurity. The crystals were cut and finished in the form of wafers  $\frac{3}{8}$  in. $\times \frac{3}{8}$  in.  $\times \frac{1}{32}$  in. The crystal orientations were determined by Laue back-reflection x-ray photographs, their surface area by low-power ( $\simeq 16 \times$ ) photomicrography.

The basic experimental technique involved use of a film containing silicon-28 and carbon-14 with an average thickness of between  $\frac{1}{4}$  and  $\frac{1}{2}$  micron. A stoichiometric mixture was made by grinding the source materials in a "diamonite" (Al<sub>2</sub>O<sub>3</sub>) mortar with glycerol. A thick paste was brushed on one surface of the samples, dried at 64°C for 24–72 h to remove glycerol, and sintered for 8 h at 1400°C (just below the melting temperature of silicon) and 2 h at 1600°C in pure argon atmosphere (55–60 cm of Hg).

The sintered samples were freed of carbon-14 activity from all five sides other than the coated side and annealed (in SiC crucibles) in a pure argon atmosphere (55–60 mm of Hg) using an induction furnace. Tungsten and graphite double susceptors were used to insure rapid heating and cooling. Sponge titanium getters were used to remove residual traces of air from the furnace atmosphere. The temperature was measured using a calibrated optical pyrometer, the readings of which were corrected for window absorption.

After the diffusion anneals each sample was weighed, counted for surface activity, and ground on all sides other than the coated side. The thickness removed was greater than the anticipated tracer penetration. The sample was then mounted on a pure boron carbide-tipped hard steel cylinder (equipped with a  $B_4C$ -tipped guard ring) and sectioned manually on a 99.999% pure aluminum block (provided with arrangements to collect the grindings with a uniform loss of about 5%) using measured amounts of pure virgin diamond powder

(obtained from Elgin National Watch Co., Elgin, Illinois). The thickness of each section was determined from the difference in sample weight before and after sectioning. The average thickness removed  $(1-3 \mu)$  was determined to an accuracy of  $\pm 0.15 \mu$ .

The collected grindings were counted for C<sup>14</sup> activity in a windowless flow counter (to a maximum accuracy of  $\pm 1.0$  counts/min). The grindings from each section were placed in a polyethylene vial and irradiated in the M.I.T. Reactor (neutron flux density  $\simeq 2.0 \times 10^{13}$ /cm<sup>2</sup> sec) for about one-half hour to convert Si<sup>30</sup> to Si<sup>31</sup> ( $T_{1/2}\cong 2.6$  h). Simultaneously, standard blank specimens were irradiated for calibration purposes and also to determine the interfering impurities introduced during sectioning operations. The irradiated product was analyzed in a 400-channel  $\gamma$  spectrometer and counted for Si<sup>31</sup> activity.

The same method was used with *p*-type polycrystalline silicon carbide (density more than 99%, grain size  $17 \mu$ ) for the determination of carbon diffusivities.

#### III. RESULTS

Silicon diffusion coefficients were determined from the  $Si^{31}$  activity of each section (calibrated against standard blanks) using the solution of Fick's second law for diffusion in a semi-infinite body with a capturing boundary and with otherwise uniform initial tracer distribution<sup>9</sup>:

$$C(x,t)/C(x,0) = \operatorname{erf} x/2(Dt)^{1/2}.$$
 (1)

These data, reported in Fig. 3, at two temperatures show poor reproducibility. This is mainly due to the large interference of 1.37-MeV disintegration from Na<sup>24</sup> and to the small range of Si<sup>31</sup> concentration in the sections (0.07 to 3.12 isotopic percent). The former interference could have been overcome by chemical separation of Si from Na in the sections (preferably before irradiation) and the latter problem can be tackled by using Si<sup>30</sup> instead of Si<sup>28</sup> as used in this study.

The concentration profiles of  $C^{14}$  in p-type silicon carbide single crystals are shown in Fig. 1; those in black polycrystalline silicon carbide appear in Fig. 2. Diffusion coefficients calculated from the linear part of each profile using the solution (diffusion from an infinitesimally thin layer into a semi-infinite body with a reflecting boundary):

$$C(x,t) = \left[ \alpha / (\pi Dt)^{1/2} \right] \exp(-x^2/4Dt)$$
(2)

are shown in Fig. 3 as a function of temperature. The carbon diffusion data in p-type SiC crystals (600 ppm aluminum) along [0001] between 1853 and 2060°C can be represented by the equation

$$D = 3 \times 10^2 \exp[(-141.5 \pm 16.6 \text{kcal})/RT] \text{ cm}^2/\text{sec.}$$
 (3)

<sup>&</sup>lt;sup>8</sup> G. Ya. Ryskin, Fiz. Tverd. Tela 1, 952 (1959) [English transl: Soviet Phys.—Solid State 1, 870 (1959)].

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Fro. 1.(a) Concentration profiles in black hexagonal silicon carbide single crystals along [0001] for diffusion of Carbon—14. (b) Concentration profiles in black hexagonal silicon carbide single crystals along [0001] for diffusion of Carbon—14.

The carbon-diffusion data for the *n*-type crystal (100 ppm nitrogen) between 1977 and 2088°C along the same direction can be represented by

$$D = 2 \times 10^{17} \exp[(-302.4 \pm 48.6 \text{ kcal})/RT] \text{ cm}^2/\text{sec.}$$
(4)

As is evident from the C<sup>14</sup> concentration profile data,



FIG. 2. Concentration profiles in six polycrystalline silicon carbode samples.

there has been some surface tie-up of the tracer atoms. Consequently, all the D values have been calculated from the linear part of the profiles at deep penetration. Since at present there is no quantitative understanding of a reasonable  $D_0$  value under this kind of impurity effect on self-diffusion (as discussed later) the ap-

effect on self-diffusion (as discussed later) the apparently high pre-exponential factor in Eq. (4) can hardly be explained. The validity of extrapolation of D values beyond the temperature where all doped



FIG. 3. Diffusion coefficients for silicon and carbon in silicon carbide as a function of temperature.

materials become intrinsic may, however, be seriously questioned.

The *p*-type material is found to have a higher diffusion coefficient than the *n*-type material within the temperature range of measurement. Also, carbon is found to be the slower diffusion species in SiC contrary to the prediction of Tomonari.<sup>10</sup>

Carbon diffusion coefficients in *p*-type polycrystalline material shown in Fig. 3 are higher than the values observed for the single crystals. This fact and the lower slopes at deep penetration on the concentration profiles (Fig. 2) are taken as evidence for more rapid diffusion at the grain boundaries, relative to the values observed in the lattice. No attempt was made to separate  $D_{ab}$ from  $D_l$ , however.

## IV. DISCUSSION

In order to attempt to assess the mechanism of diffusion of carbon, the characteristics are compared with the more intensively investigated behavior in germanium and silicon with modifications based on known properties.

The pertinent facts are:

(1) Vacancies in germanium are electron acceptors<sup>2,11-16</sup> with an energy level 0.2 eV above the valence band.

(2) Vacancies in silicon are mostly neutral with slight acceptor character (0.16 eV below the bottom of the conduction band).2,17

(3) Vacancies in diamond are virtual donors (hole traps).18

(4) SiC is intermediate in properties between silicon and diamond<sup>19</sup>; the carbon vacancies are assumed to be virtual donors.

(5) The change in self-diffusion coefficients in germanium with doping has been attributed to the change in Fermi level.<sup>4</sup> The self-diffusion coefficient in p-type is lower than in *n*-type germanium.

(6) A vacancy mechanism is shown to operate in self-diffusion and substitutional impurity (mainly Group III acceptors and Group V donors) diffusion in both silicon and germanium.<sup>2,3</sup>

(7) In SiC both boron (acceptor) and nitrogen (donor) occupy carbon lattice sites<sup>20</sup>; we assume that Al also occupies carbon lattice sites.

The data above show that in the temperature range of measurement carbon diffusion in SiC is more rapid in p-type (Al-doped) than in n-type (N-doped) material, which is the opposite of the behavior observed in germanium. This is attributed to the reversal in electrical character of lattice vacancies (from acceptor in Ge to virtual donor of C lattice vacancy in SiC). We conclude that the carbon self-diffusion in SiC probably occurs by a vacancy mechanism.

The more rapid diffusion of Si than C is not understood. Swalin<sup>2</sup> has shown a multiplicity of energy terms which must be considered for understanding the diffusion behavior in elemental semiconductors when impurities are present. The case for the compound semiconductor is more complex. Very recently, energy of formation of point defects in Group IV semiconductors has been calculated.<sup>21</sup> There is less information on the relative energies involved in the vacancy equilibria for both Si and C in SiC. In addition, the energy involved in substitutional disorder in SiC is assumed to be in the same range as the energy involved in vacancy formation. Hence the relative contributions of: (a) neutral vacancies, (b) charged vacancies, (c) impurityimpurity complexes, (d) vacancy-impurity complexes, and (e) substitutional disorder in the respective lattices to the self-diffusivities cannot be identified with the data presently available. But charged vacancies and vacancy-impurity complexes seem to be the dominating factors in carbon self-diffusion in SiC.

### **V. CONCLUSIONS**

The diffusion coefficients in SiC are greater for Si than for C. The diffusion coefficients for carbon are greater in p-type (Al-doped) than in n-type (N-doped) SiC. In available materials the carbon diffusivity is impurity type and level controlled. Carbon appears to diffuse by a vacancy mechanism.

#### **ACKNOWLEDGMENTS**

This work was supported by the Office of Naval Research under Contract No. 1841(82).

The authors are thankful to Dr. J. Hornstra, of the Philips Research Laboratories, Eindhoven, The Netherlands, for providing several impurity-controlled and pure SiC crystals, and to Dr. T. Vasilos, of the Avco Corporation, Wilmington, Massachusetts, for supplying polycrystalline SiC used in this work.

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