Self-diffusion of ^{14}C in polycrystalline β-SiC

M. H. HON[†], R. F. DAVIS
Department of Materials Engineering and Engineering Research Services Division,
North Carolina State University, Raleigh, North Carolina 27650, USA

The ^{14}C self-diffusion coefficients for both lattice (D_{lc}^{*}) and grain boundary (D_{bc}^{*}) transport in high purity CVD β-SiC are reported for the range 2128 to 2374 K. The Suzuoka analysis technique revealed that D_{bc}^{*} is 10^5 to 10^6 faster than D_{lc}^{*}; the respective equations are given by

$$D_{lc}^{*} = (2.62 \pm 1.83) \times 10^8 \exp\left\{-\frac{(8.72 \pm 0.14)\,\text{eV/atom}}{kT}\right\} \text{cm}^2\,\text{sec}^{-1}$$

$$D_{bc}^{*} = (4.44 \pm 2.03) \times 10^7 \exp\left\{-\frac{(5.84 \pm 0.09)\,\text{eV/atom}}{kT}\right\} \text{cm}^2\,\text{sec}^{-1}$$

A vacancy mechanism is assumed to be operative for lattice transport. From the standpoint of crystallography and energetics, reasons are given in support of a path of transport which involves an initial jump to a vacant tetrahedral site succeeded by a jump to a normally occupied C vacancy.

1. Introduction

Silicon carbide exists in two principal modifications: the α form which encompasses a large number of hexagonal or rhombohedral polytypes and the β form which crystallizes in the cubic zincblende structure. The primary classical uses of this material have been for abrasives, refractories and heating elements in electric furnaces. However, with the advent of significant advances in the sintering of both β- and α-SiC to essentially theoretical density by Prochazka [1] and Coppola and McMurtry [2], respectively, coupled with and stimulated by recent governmental and industrial funding, primarily in the area of high temperature engine technology; additional employment of this material in previously unimagined applications appears imminent.

The knowledge that diffusion processes play major roles in almost all powder densification, grain growth and high temperature deformation mechanisms in ceramic materials coupled with the growing commercial interest in β-SiC, the fact that no prior self- or impurity diffusion studies have

been conducted on β-SiC and the availability of high purity fully dense and undoped material (no single crystals of suitable size currently exist) prompted the authors to perform the research described herein.

The only previous directly related research has been the ^{14}C self-diffusion studies in α-SiC by Ghostagore and Coble [3] and more recently by Hong [4] and Hong and Davis [5]. The former authors found that D_c^{*} in p-type (Al doped) single crystals was higher than in the n-type (N-doped) crystals. Furthermore, D_c^{*} in p-type polycrystalline α-SiC was higher than in the analogous single crystals and was attributed to a grain boundary contribution in the former; however no effort was made to separate this contribution from the volume diffusion. Hong [4] showed that D_c^{*} in high purity, essentially intrinsic α-SiC single crystals is higher than in n-type (N-doped) crystals grown by the same procedures. Supplementary impurity (B, Be, Al, Ga, and N) diffusion research [6] has also been conducted in α-SiC, but not in the β form. These studies support the conclusions of the

self-diffusion work in that (1) all substitutional species diffuse by a vacancy mechanism, (2) that C and Si vacancies possess donor and acceptor character, respectively, and (3) the numbers of each vacancy type and therefore the diffusion coefficient of the element under study can be altered by the presence of certain impurities.

The following details the results of the first reported study concerned with the understanding of both volume and grain boundary diffusion of C in β-SiC. A similar ongoing programme involving the self-diffusion of Si in this material will be reported at a later date.

2. Experimental procedure

The polycrystalline β-SiC employed in this research was commercially* produced by the initial pyrolysis of methyltrichlorosilane ($CH_3 SiCl_3 \rightarrow$ $SiC + 3HCl$) at 1673 K and the subsequent chemical vapor deposition (CVD) and reaction of C and Si on a square graphite substrate. The final volume (5.1×10^{-2} m by 9.5×10^{-3} m thick) of material was annealed in purified Ar at 10.34 MPa and 2373 K to remove residual stresses.

Spectrochemical and thermal neutron activation analyses of 21 impurity elements commonly found in SiC revealed that, except for the metals derived from the crushing operation, only Cu (60 p.p.m.) was present as a minor impurity. No significant amounts of the commonly introduced n- or p-type elements such as N, B or Al were contained in the samples as was also evident by the $\simeq 5 \times 10^4$ Ω cm electrical resistivity. Because of this low impurity content Hall measurements of the charge carrier concentration were not successful. The presence of additional polytypes was determined by X-ray diffraction using Ni-filtered $CuK\alpha$ radiation; only a trace of the alpha hexagonal 15R polytype was detected in the predominantly β(3C) material. Density values on samples cut from four different portions of the as-received pieces were measured to be $(3.213 \pm 0.005) \times 10^3$ kg m^{-3} which is close to the 3.210×10^3 kg m^{-3} value reported for single crystals of pure β-SiC [7]. This, coupled with the microstructural evidence described below, strongly indicates that the initial deposit is theoretically dense.

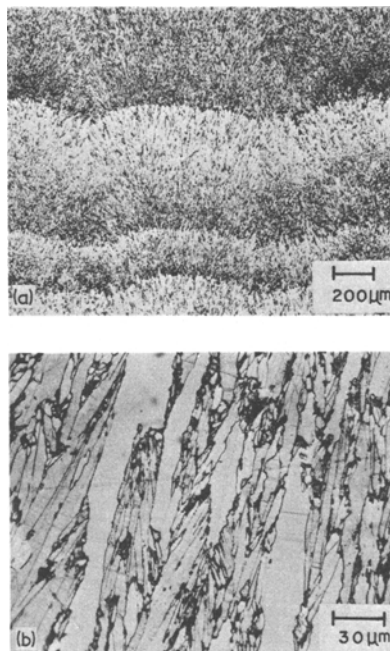The microstructural features pictured in Fig. 1 were revealed using a molten salt etch†, similar to

Figure 1 Microstructure of the polycrystalline β-SiC taken at two different magnifications from a section cut parallel to the growth direction. Tracer diffusion was perpen- to the pictured surface.

that employed by Shaffer [10], at a temperature of 873 K for 4.3 to 7.2×10^3 sec using a 10^{-4} m^3 $Al_2 O_3$ crucible. The ^{14}C tracer was deposited on and diffused perpendicular to the surface which is pictured. The lower magnification picture of Fig. 1a shows that the microstructure of this material is composed of $\simeq (1 \times 0.5) \times 10^{-10}$ m^2 irregular crystals and an equal proportion of lighter transparent bands composed of longer and larger ($(5.0 \times 1.0) \times 10^{-10}$ m^2 to $(25.0 \times 2.5) \times 10^{-10}$ m^2). The latter shape is common in the CVD growth of materials; whereas, the former results most frequently from abrupt fluctuations in feed gas flow or temperature. Transport studies conducted at the outset of the programme described herein, using excised sections prepared as described below and containing only one or the other of the above microstructures, revealed no differences in the values of the diffusion coefficient between the two parts of the samples. No evidence of dislocations was revealed by the etching procedure.

The rough surface texture of the as-grown bulk pieces was diamond ground away and the resulting

material cut into square (6.35 × 10⁻³ m on a side) diffusion samples having a thickness range of 5.0×10^{-4} to 1.0×10^{-3} m with resulting faces which were parallel to the growth direction. Diamond lapping with a double-faced eccentric system* was employed to produce a 1×10^{-6} m finish on both top and bottom sample surfaces, a flatness within two light bands of He and a parallelism of 2×10^{-6} m between the two surfaces.

The Si^{14}C tracer material was produced from -325 mesh powders of natural Si and diluted ^{14}C wet-mixed in glycerol in a Si/C ratio of 1.2, brushed on a "source" crystal and heated to 1723 K for 14.4×10^3 sec and 1823 K for 7.2×10^3 sec under 8.1×10^4 Pa of Ar to form β-SiC. The as-formed tracer powder was subsequently deposited on a second "seed" crystal by a technique known as the travelling solvent method (TSM) wherein a SiC–metal, tracer–SiC sandwich configuration is heated in a thermal gradient such that the metal (Y in this research) is melted and dissolves the tracer which precipitates on and chemically bonds to the colder SiC substrate. The subsequent formation of a 0.25 to 0.5×10^{-6} m tracer layer satisfied the boundary conditions for the thin-film solution to Fick's second law. In addition, the ratio of diffusion depth to film thickness was $\simeq 60:1$. Complete descriptions of the utilization of TSM in this research are given in references [11, 12].

The tracer-containing samples prepared as described above were covered by a second β-SiC piece of similar size to mitigate the vaporization of Si from the tracer, placed in a graphite crucible coated with SiC on the inner wall, surrounded by high purity β-SiC and Si powders to create an atmosphere rich in Si which further prevented the loss of Si from the tracer and the transformation of the β-SiC to one or more of the α forms.† The covered crucible and samples were heated in a graphite furnace‡ in high purity static (9×10^4 Pa) Ar to 2073 K followed by rapid heating to the selected diffusion temperature within the range of 2128 to 2374 K. The temperature was checked frequently using a calibrated optical pyrometer and the furnace monitored electronically and graphically for any drift in the power output. The absorption of the sight glass was also taken into account. Because of the use of a graphite furnace and crucible, black-body conditions were extant, and no temperature correction for emissivity was required. A total variation of ±7 K during the run was possible because of practically thermostatic watercooling.

Following a rapid cooling period, the edges of the samples were ground to eliminate any penetration caused by surface diffusion and mechanically sectioned using equipment of a design described in [13]. The collected grindings (92 ± 1% efficiency [13]) were coated with colloid, dried in stationary air and placed into a proportional counter containing a thin Al window which was continuously flushed with P-10 gas. The 1.9 kV anode voltage employed was approximately at the centre of the beta plateau for the 0.155 beta radiations in the assembly. The average accuracy of the determination of the penetration distance of each section was 1.5×10^{-7} m.

The solutions derived by Fisher [14] and Suzuoka [15] are the principal equations used by investigators for calculating the grain boundary diffusion coefficients from experimental data. Fisher's equation was derived assuming a constant tracer source and involves several approximations which cause it to be relatively inexact; the solution indicates that the log of the concentration (C') of the diffusing species in the faster transport boundary portion of the total profile should be linearly proportional to the first power of the distance, x. Although Levine and MacCallum [16], using fewer approximations, have shown that the power of x should be 6/5, the simpler Fisher relationship is still the most commonly used and was also employed in the research described herein for comparison with the more accurate Suzuoka solution. This latter equation also incorporates very few assumptions, was derived for a thin-film tracer source such as that employed in the present research and again shows that the plot of log C' versus $x^{6/5}$ should be linear for grain boundary diffusion.

3. Results and discussion
3.1. Diffusion profiles
Representative diffusion profiles plotted as the log

---

*Unipol PA-500, Geos Company, Stamford, Connecticut 06902, USA.
†The possible occurrence of this transformation during the diffusion anneals was investigated before and during the diffusion research; however, no change in the amounts or the forms of the polytypes from that of the as-received samples was detected by X-ray diffraction.
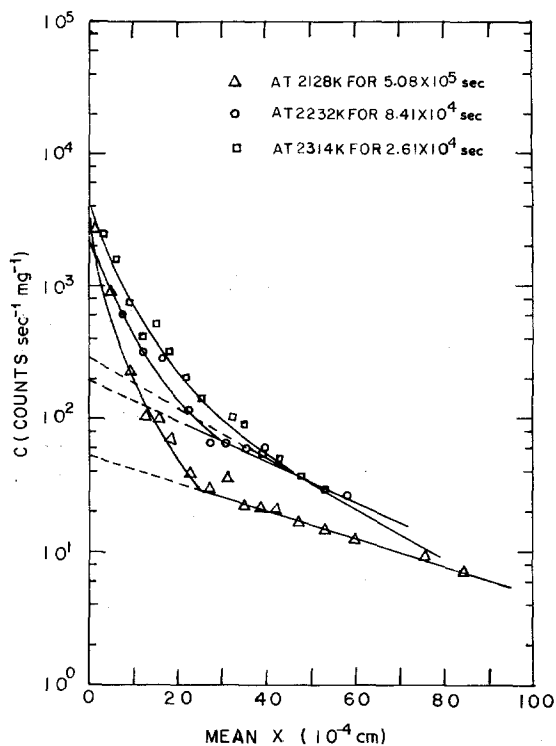‡Model 10-2.5 × 4 G-0-25, Centorr Associates, Inc., Suncook, New Hampshire, USA

Figure 2 Representative ^{14}C diffusion profiles in polycrystalline β-SiC plotted as a function of x in order to use Fisher's solution to calculate coefficients of grain boundary diffusion.

Figure 3 Representative ^{14}C diffusion profiles in polycrystalline β-SiC plotted as a function of $x^{6/5}$ in order to employ Suzuoka's equation to calculate coefficients of grain boundary diffusion.

of the total specific activity (C) of ^{14}C versus x (Fisher model) and $x^{6/5}$ (Suzuoka model) are shown in Figs. 2 and 3, respectively. All profiles consist of three regions: (1) a deep linear section which represents the grain boundary diffusion, (2) a fairly long intermediate section containing contributions from both grain boundary and volume diffusion and (3) a short ($\simeq 2 \times 10^{-6}$ m) "near surface" high gradient, high activity section. A discussion of each of these sections is given below.

Concerning the deep linear section, it has been stated by Shewmon [17] that only beyond the diffusion distance $4(D_1 t)^{1/2}$ (D_1 = lattice diffusion coefficient), can the diffusion profiles be considered to be produced solely by grain boundary transport. This reasoning was also used in the present study where it was found that $4(D_{1c}^* t)^{1/2} \simeq 30 \times 10^{-6}$ m in the temperature range of interest. Grain growth was not observed to occur during the diffusion anneals.

Fisher [14] has derived a simplified equation for diffusion along a straight boundary from a constant source in which
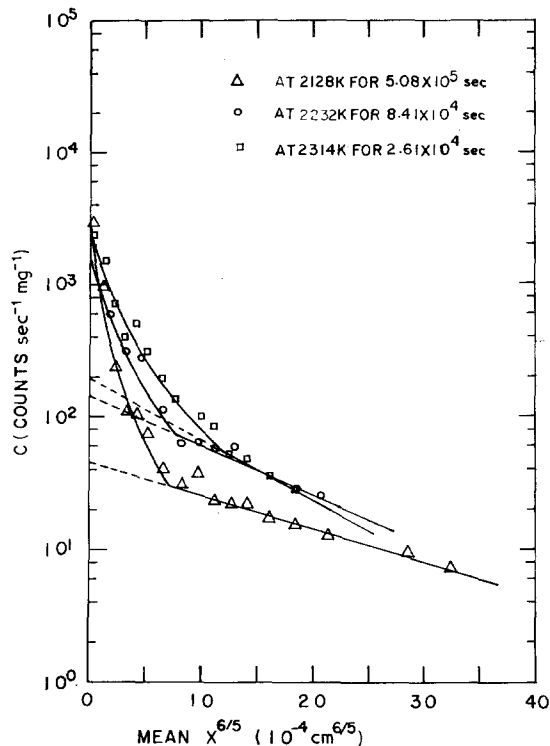
$$\frac{d \log C'}{dx} = -2^{1/2} (D_1/D_b \delta)^{1/2} \log e/(\pi D_1 t)^{1/4} \quad (1)$$

where C' is the tracer concentration in the grain boundary portion of the profile at a distance x, D_1 and D_b are the volume and the grain boundary diffusion coefficients, respectively, δ is the grain boundary width and t is the annealing time. The slopes of these portions of the curves of Fig. 2, when substituted for $d \log C'/dx$ yield the values of $(D_{1c}^*/D_{bc}^* \delta)^{1/2}$ whereby D_{bc}^* can be calculated if D_1 and δ are known.

As noted above, because a thin film source was actually used in this study, the Suzuoka [15] solution was also employed to evaluate the grain boundary diffusion coefficients. The equation given by Suzuoka for numerical calculations of the grain boundary diffusion coefficient is

$$0.973 \log\left(\frac{D_b}{D_1} - 1\right) =$$

$$6.567 - 1.644 \log\left\{\frac{-d\log C'}{d(x^{6/5})} - \log(D_1 t)^{1/2}\right\} \quad (2)$$

TABLE I Volume and grain boundary diffusion coefficients of ^{14}C in polycrystalline β-SiC

Specimen number	Annealing temperature (K)	$1/T \times 10^4$ (K^{-1})	Annealing time (sec)
B-605	2128	4.70	5.08×10^5
C-704	2200	4.55	2.58×10^5
B-609	2232	4.48	8.41×10^4
B-608	2274	4.40	4.45×10^4
B-602	2314	4.32	2.61×10^4
B-315	2374	4.21	1.08×10^4

Specimen number	D_{lc}^* (Fisher) (cm^2 sec^{-1})	D_{lc}^* (Suzuoka) (cm^2 sec^{-1})	D_{bc}^* (Fisher) (cm^2 sec^{-1})	D_{bc}^* (Suzuoka) (cm^2 sec^{-1})
B-605	$(8.81 \pm 0.89) \times 10^{-13}$	$(9.80 \pm 1.45) \times 10^{-13}$	$(3.90 \pm 0.20) \times 10^{-7}$	$(6.78 \pm 0.35) \times 10^{-7}$
C-704	$(2.04 \pm 0.22) \times 10^{-13}$	$(1.98 \pm 0.12) \times 10^{-12}$	$(8.67 \pm 1.19) \times 10^{-7}$	$(1.52 \pm 0.22) \times 10^{-6}$
B-609	$(4.68 \pm 0.11) \times 10^{-12}$	$(5.17 \pm 0.13) \times 10^{-12}$	$(1.46 \pm 0.20) \times 10^{-6}$	$(2.52 \pm 0.33) \times 10^{-6}$
B-608	$(1.08 \pm 0.09) \times 10^{-11}$	$(1.16 \pm 0.04) \times 10^{-11}$	$(2.20 \pm 0.11) \times 10^{-6}$	$(4.32 \pm 0.24) \times 10^{-6}$
B-602	$(2.06 \pm 0.16) \times 10^{-11}$	$(2.19 \pm 0.14) \times 10^{-11}$	$(3.27 \pm 0.40) \times 10^{-6}$	$(6.32 \pm 0.75) \times 10^{-6}$
B-315	$(5.63 \pm 0.65) \times 10^{-11}$	$(6.09 \pm 0.44) \times 10^{-11}$	$(7.65 \pm 0.25) \times 10^{-6}$	$(1.62 \pm 0.04) \times 10^{-5}$

Grain boundary diffusion coefficients calculated from these profiles using both the Fisher and Suzuoka solutions; as well as the values of D_{lc}^* obtained from these curves, as described below; and the value of δ used by Fisher and Suzuoka ($= 5 \times 10^{-10}$ m) are given in Table I and plotted in Fig. 4 as a function of $1/T$.

The resulting curves can be expressed as

$$D_{bc}^* = (1.27 \pm 0.57) \times$$
$$10^7 \exp\left(\frac{-5.72 \pm 0.09 \text{ eV/atom}}{kT}\right) \text{cm}^2 \text{ sec}^{-1}$$
(Fisher solution) \hfill (3)

$$D_{bc}^* = (4.44 \pm 2.03) \times$$
$$10^7 \exp\left(\frac{-5.84 \pm 0.09 \text{ eV/atom}}{kT}\right) \text{cm}^2 \text{ sec}^{-1}$$
(Suzuoka solution) \hfill (4)

From this data, it may be seen that the Fisher analysis yields values of D_{bc}^* which are 42% lower than those obtained from the Suzuoka analysis; however, the corresponding activation energies, Q_b, are nearly identical. It is strongly believed by the present writers that the values of D_{bc}^* calculated using the Suzuoka equation are more accurate because the latter's own use of the thin film solution and the small number of assumptions employed in the derivation.

There are, however, some problems in the use of either the Fisher or the Suzuoka equations in the calculations of D_b which could not be overcome with the β-SiC samples of this research. For instance, in these equations the grain size and, therefore, the length of the grain boundary is assumed to be much larger or longer than the value of diffusion depth. Furthermore the grains are assumed to be uniformly distributed throughout the crystal. These assumptions are obviously not true for the β-SiC used in this study. A final, rather important point is that both analyses and calculations yield only the product $D_b\delta$, and, therefore
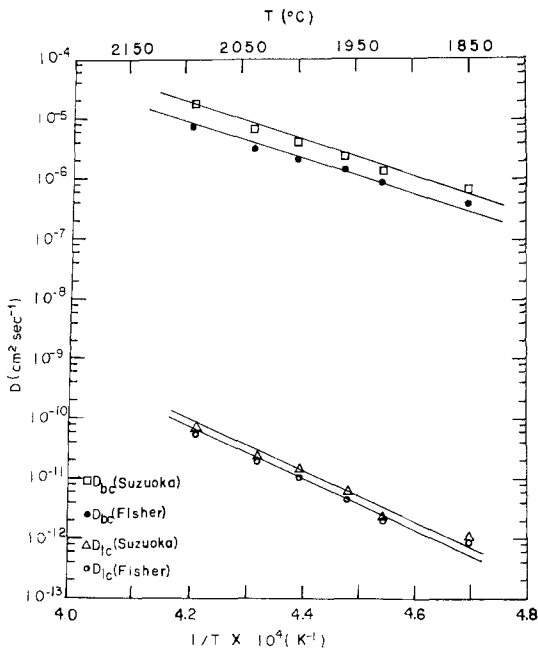

Figure 4 Self-diffusion coefficients for ^{14}C lattice and grain boundary diffusion, calculated by the Fisher [14] and the Suzuoka [15] equations, as a function of $1/T$.

an "effective" grain boundary width, δ, must be assumed. Because of mathematical difficulty, all theoretical treatments of this problem have assumed a discontinuous change in diffusivity from D_b to D_1 at a distance $\delta/2$ from the centre of the boundary. The effective width, δ, of the high diffusivity path is therefore somewhat difficult to accurately determine. However, the error introduced in assuming a reasonable δ value should not affect the activation energy unless δ is influenced by temperature. In the small 2128 to 2374 K range used in this research, this is considered unlikely.

The intermediate section of the ^{14}C profiles beginning at $\simeq 2 \times 10^{-6}$ m and extending to $\simeq 25$ to 45×10^{-6} m, depending on the temperature and time at temperature, are composed of both volume and grain boundary contributions to diffusion. In order to evaluate the volume diffusion coefficients, a graphical method employed by Sze and Wei [18] and Lundy and Federer [19] has been used to separate these two contributions. This method is based on the assumption noted above that for unidirectional diffusion from a plane

source of radioactive material, the penetration of the tracer beyond a distance of $\simeq 4(D_1 t)^{1/2}$ into the specimen from the source is caused solely by grain boundary effects. This, in turn, is based on the assumption that within the temperature range employed, the D_b/D_1 ratio is always very large ($\geqslant 5 \times 10^4$). The initial step in this determination involves the extension of the straight line segments in Figs. 2 and 3 to the y axis. If $y_1(x)$ and $y_1(x^{6/5})$ represent the total tracer activities in the middle portion of the curves produced from consideration of the Fisher and Suzuoka models, respectively, and $y_2(x)$ and $y_2(x^{6/5})$ represent the analogous activities for the two models on the extended line, then, $\Delta y = y_1 - y_2$ in these two sets of values may be taken as the tracer activities resulting only from volume diffusion. These new concentration values, Δy, are plotted against the square of the penetration distance for each profile. If such a plot gives a straight line as shown in Figs. 5 and 6, the diffusion coefficients calculated from these profiles are equal to D_1.
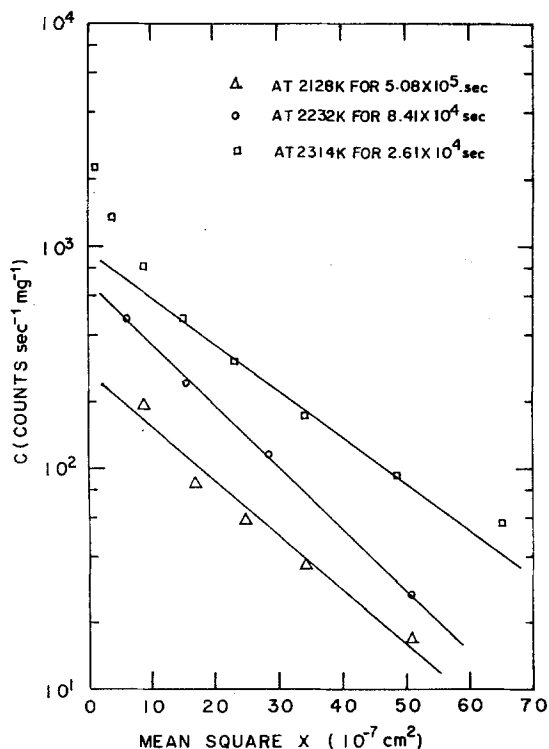
The volume diffusion coefficients subsequently

Figure 5 Representative ^{14}C diffusion concentration profiles in polycrystalline β-SiC obtained by subtraction of the extrapolated grain boundary concentration values from the total concentration values in the graphs obtained from a consideration of Fisher's model.

Figure 6 Representative ^{14}C diffusion concentration profiles in polycrystalline β-SiC obtained by subtraction of the extrapolated grain boundary concentration values from the total concentration values in the graphs obtained from a consideration of Suzuoka's model.
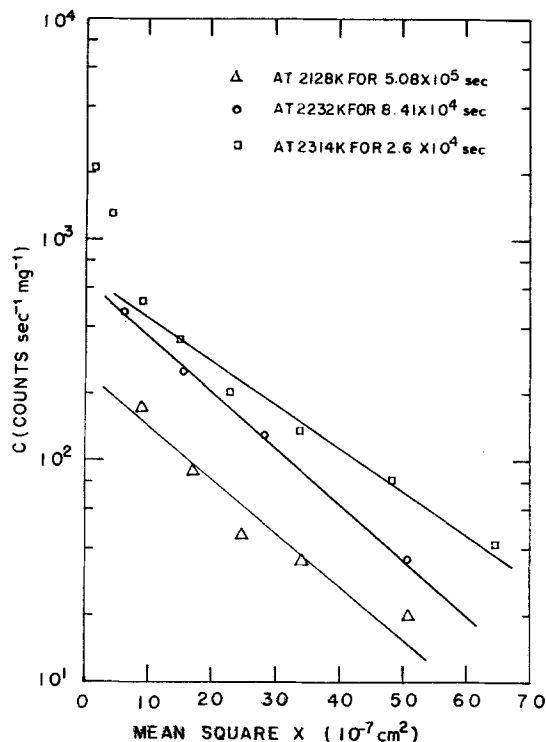
determined from the linear profiles of Figs. 5 and 6 using the thin film solution to Fick's second law are given in Table I and plotted in Fig. 4 as a function of $1/T$. The resulting curves can be expressed as follows:

$$D_{1c}^* = (1.97 \pm 1.50) \times 10^8 \exp\left(\frac{-8.67 \pm 15 \text{ eV/atom}}{kT}\right) \text{cm}^2 \text{ sec}^{-1}$$

(Fisher)   (5)

$$D_{1c}^* = (2.62 \pm 1.83) \times 10^8 \exp\left(\frac{-8.72 \pm 0.14 \text{ eV/atom}}{kT}\right) \text{cm}^2 \text{ sec}^{-1}$$

(Suzuoka)   (6)

A perusal of this data reveals that the pre-exponential (D_0) and activation energy (Q) values determined from both the Fisher and Suzuoka curves are within the calculated standard deviations of each other. The accuracy of the valuation of the ^{14}C volume diffusion in β-SiC by this separation method is not known as the volume diffusivities in single crystal β-SiC are not available. However, Suzuoka [15] has estimated from literature values of volume diffusion determined directly on single crystals and by the separation technique on poly-crystalline specimens of the same material that the diffusivities from the latter technique almost always overestimate the single crystal value by $\simeq 10\%$. The reason for this difference has been attributed by Sze and Wei [18] to the fact that grain boundaries act as internal sources of vacancies which can, in turn, enhance diffusion by an additional vacancy mechanism.

Although not visible in all profiles, the presence of a section near $X = 0$ wherein the concentration increases rapidly is observed (see the profiles for 2314 K in Figs. 5 and 6) and is often referred to as the "near-surface" effect (NSE). Though many theories for this behaviour have been proposed [20–22], the reasons appear to be dominated by sample conditions and tracer deposition techniques. Lundy and Padgett [22], in a direct study of this phenomenon in ^{60}Co diffusion in Ag, concluded that the most probable reason was the surface segregation of the ^{60}Co atoms in order to lower the surface energy. Other possible causes promulgated for the NSE include (1) poor tracer deposition and/or the presence of an oxide film [23], (2) the accumulation in single crystals, via

dislocations at or near the surface, of super-saturated vacancies entrapped during cooling [24], (3) surface roughness [25], (4) strain arising from sample preparation [6], and (5) a "delayed tracer effect" wherein non-ideal thin-film boundary conditions are created by the tracer deposition method, the tracer atoms continue to enter the specimen as a function of time and this section of the profile is lengthened as the time of the anneal increases [20].

In the present work, the use of the oxidant Y (which is insoluble as an impurity in SiC) in the TSM produced an oxide-free layer; the dislocation density was apparently very low and, in diffusion anneals conducted at the same temperature for varying lengths of time, the distance of the surface effect did not increase with time. Thus, several of the above reasons are eliminated as potenial causes of this effect. However the lapping procedure used to produce optically smooth surfaces on the β-SiC samples also caused sub-surface damage in the form of randomly oriented scratches of various depths (maximum $= 3 \times 10^{-6}$ m). It is concluded that surface vacancies in these flaws could serve as trapping sites for the ^{14}C or the surfaces and volume could hold decreasing amounts of Si^{14}C as one moved closer to the crack tip. This decrease in trapping ability as a function of crack depth could translate into a sharp drop in the concentration profile.

A final point which is relevant to the above is that of decomposition. Considerable effort was expended in this programme to discern the effect of this phenomenon in the values of the diffusion coefficient, as reported in [21]. Although important for Si transport [26], in the case of the more rapid C diffusion, the ratio $Vt/(D_{1c}t)^{1/2}$ was approximately 0.06, where $V =$ rate of change of surface position. Dawson et al. [27] have shown that as long as this ratio $\leqslant 0.04$, the value of D_1 will not be in error by more than 5% if sample evaporation is neglected. The ratio $(Vt/D_{bc}t)^{1/2} \simeq 8.0 \times 10^{-5}$ and correction in this case was also not made.

3.2. Pre-exponential constant and activation energy

Previous experimental data obtained from both impurity and self-diffusion studies in SiC reveal that the transport in each case most probably involves the movement of the atom to a normally filled vacant site on its own sublattice. Several

investigators [28-32] have determined that the impurities of N [28-32] and B [28, 31, 32] are found only on the three nonequivalent C sites, while Al [30] occupies only the Si sites. This has received confirmation from impurity diffusion research, as reviewed by Vodakov and Mokhov [6], in that the presence of other impurities introduced during growth affects the vacancy concentrations on each sublattice and therefore measureably affects diffusion of a second externally introduced impurity.

A vacancy mechanism has also been concluded to be operative in ^{14}C self-diffusion in α-SiC. Ghoshtagore and Coble [3], showed that the D_c^* in p-type SiC is greater than that in n-type material and proposed a mechanism in which the number of charged (ionized) C vacancies and, therefore, the total number of C vacancies is governed by the type and concentration of impurity dopant. Hong [4] has confirmed this hypothesis by showing that the presence of N donors decreases and increases the D_c^* and D_{Si}^* respectively, relative to that found in pure crystals.

From the existing vacancy mechanism interpretation of impurity and self-diffusion described above for α-SiC and the diffusion activation energy calculations described below, it is proposed by the present authors that ^{14}C self-diffusion in β-SiC also occurs by a vacancy mechanism.

The order of magnitude of the value of the activation energy for ^{14}C self-diffusion obtained in this study appears to support a vacancy transport mechanism in polycrystalline β-SiC. The C vacancy formation energy may be estimated following the same argument as Dienes [33]. Four Si-C bonds are broken removing one atom to the surface. This requires an initial expenditure of energy of 3.0 × 4 = 12.0 eV/atom, where 3.0 eV/atom is the C-Si bond strength determined by Pauling [34]. In placing an atom on the surface, however, two bonds are formed resulting in an energy gain of (6.0 eV/atom). The energy required to form a vacancy, ΔH_f, is therefore estimated to be 6.0 eV/atom. From the migration energy of C diffusion in graphite, Gohshtagore [23] has estimated that 2.6 eV/atom or more should be required for the motion of a C vacancy in SiC. This makes a total 8.60 eV/atom or more required for the self-diffusion of ^{14}C in SiC, in good agreement with the experimental results ($Q_{lc} = 8.72$ eV) of this study.

The activation energy for ^{14}C grain boundary

diffusion in β-SiC is 66% of the corresponding value for ^{14}C volume diffusion. Although a correlation between these two modes of diffusion is difficult to determine, Gifkins [35], borrowing on previous reports of theoretical and experimental research, has made an attempt through the use of a model for grain boundary diffusion having two limiting extremes. The overall model predicted by Gifkins depicts a grain boundary structure of islands composed of atoms which have varying degrees of "good" atomic fit within each other and which are separated by channels of relaxed vacancies. From this overall structural description, two limiting cases, were characterized. (1) If the atomic fit within the islands is very good, almost all the grain boundary will be associated with the channels between the islands. On the other hand, (2) the atomic fit within the islands may be so poor that almost all the energy is associated with internal atom-atom strains, possibly extending into the neighbouring crystals. In the former case, all the grain boundary energy was assumed by Gifkins to be associated with channels of vacancies which allowed ease of atomic transport along them. The activation energy of grain boundary diffusion, Q_b, was calculated in this case to be 0.5 of the volume diffusion activation energy, Q_1. In the latter case, all the grain boundary energy was assumed to be present only as strained atom-atom bonds, which would act to reduce both the formation and the migration of vacancies. As such Q_b was predicted to be 0.8 of Q_1. As pointed out by Gifkins it is reasonable to believe that a compromise structure should exist between these two limiting cases with the actual Q_b having values between 0.5 and 0.8 Q_1. The available data for several materials as well as that for ^{14}C self-diffusion in β-SiC in this research agrees with this conjecture in that $Q_b = 0.66 Q_1$.

Zener [36] has developed an empirical equation for calculating ΔS, the entropy for a vacancy mechanism of diffusion which is based on the elastic strain established in the lattice as an atom moves from one point to the next. This equation is given by

$$\Delta S = \lambda \beta \frac{\Delta H}{T_{mp}} \qquad (7)$$

where λ is a constant equal to 0.55 for self-diffusion in f c c metals, T_{mp} = melting point of the solvent (vacancies are the solute in the case of self-

diffusion) and β is a constant equal to (T_{mp}/μ_0) $(d\mu/dT)$, where μ and μ_0 are the elastic shear moduli at a given temperature T and 0 K, respectively. Neither the shear nor bulk moduli are known as a function of T in SiC; however, the value of β for a variety of metals ranges from 0.25 to 0.45 with 0.35 being a good average and the one employed below. Equation 7 therefore becomes

$$\Delta S = 0.193 \frac{\Delta H}{T_{mp}} \qquad (7a)$$

Equation 7a shows that ΔS is proportional to ΔH, i.e., the activation energy of diffusion. Therefore, as a large activation energy was determined for volume diffusion in β-SiC in this study, a large ΔS is thus also expected. Since the D_0 value is exponentially proportional to ΔS, it is also reasonable to expect the large D_0 value which was experimentally obtained.

3.3. Crystallographic mechanism of C diffusion

The zincblende structure of β-SiC, Fig. 7, is formed by the interpenetration of the fcc lattices of Si and C. The Si atomic positions in this material are

○ Si ATOM

● C ATOM

○ C VACANCY

✕ OCTAHEDRAL SITE

✕ TETRAHEDRAL SITE

Figure 7 Beta-SiC unit cell for illustrating the possible paths of C diffusion.

at $0\,0\,0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$ which, in turn, produces four octahedral sites which remain vacant and eight tetrahedral vacancies of which half are filled by $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ plus each Si position. These vacant sites may now be used as intermediate positions for ^{14}C diffusion from one normally filled structural position to another.

Using the Si covalent radius of 1.17 Å and the β-SiC lattice parameter = 4.36 Å, the "effective" radii of the octahedral and tetrahedral sites were determined to be 1.01 Å and 0.8 Å, respectively. From a consideration of the covalent radius of C ($r_c = 0.77$ Å), it is obvious that this atom would have no problem in occupying either type of void. Since this is a cubic material, the diffusion mechanism is the same in any direction. Thus, for illustrative purposes, C transport may be arbitrarily chosen to occur along the y direction as shown in Fig. 7. Geometrical considerations of the restraint on this movement as a function of the choice of the succeeding atomic site(s) to be occupied indicate that this atom, e.g., the one labelled E diffuses initially to the normally unfilled C vacancy at G, resides momentarily at this position and moves to a normally filled vacant position at, e.g., J. In following this path, the C atom leaving the E position must pass between two Si to reach G and two additional Si to reach J.

An alternative route is E—H—J, where H is a normally filled vacant C position. However in this route, the C atom must pass through three Si atoms to H and three more Si to reach J. Although the atom at E now has a choice of three equivalent sites to which to jump, including H, to accomplish the same distance of movement, (compared to only one equivalent site at G), two other C atoms on the same plane as E may also be competing for the H position.

A third possible transport path is E—B—J, where B is an octahedral site. However, using this path, the C atom would encounter approximately three atoms in getting to B and three more in getting to J. The activation energy of motion in these last two paths should exceed that of the E—G—J route. The curves of D versus $1/T$ indicate only one activation energy for bulk diffusion and therefore imply only one mechanism of transport; from a consideration of the amount of Si dilation necessary to allow the C atoms to reach a site such as J one unit cell away, the path through the normally unfilled tetrahedral site appears to be the easiest and therefore the lowest in energy.
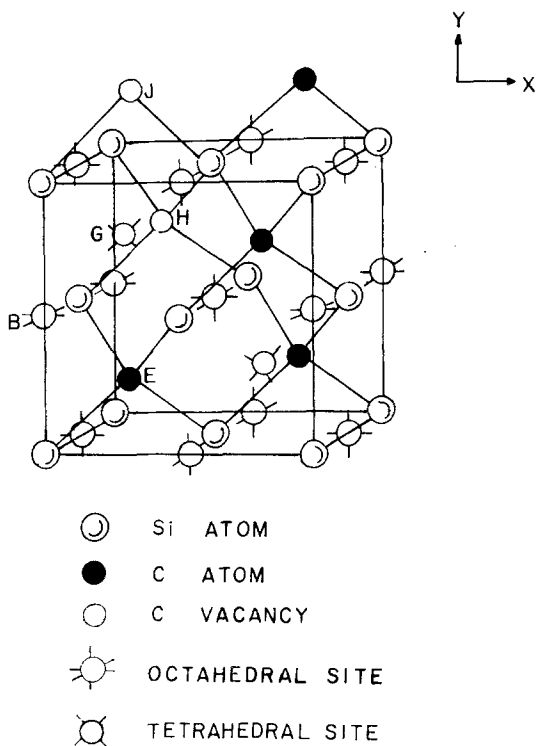
4. Conclusions

(1) The Suzuoka analysis for diffusion from a thin-film tracer source into a polycrystalline material provides the more accurate values for the coefficients of ^{14}C lattice (D_{lc}^*) and grain boundary (D_{bc}^*) transport in β-SiC. The values of these coefficients are given by

$$D_{lc}^* = (2.62 \pm 1.83) \times$$

$$10^8 \exp\left(\frac{-(8.72 \pm 0.14)\,\text{eV/atom}}{kT}\right)\,\text{cm}^2\,\text{sec}^{-1}$$

$$D_{bc}^* = (4.44 \pm 2.03) \times$$

$$10^7 \exp\left(\frac{-(5.84 \pm 0.09)\,\text{eV/atom}}{kT}\right)\,\text{cm}^2\,\text{sec}^{-1}$$

The common Fisher analysis leads to grain boundary diffusivities which are an average of 42% lower than the above; however, the lattice diffusivities calculated by this method are an average of only 6% less.

(2) D_{bc}^* in β-SiC is larger than D_{lc}^* by a factor of 10^5 to 10^6, depending on the temperature. Furthermore, the activation energy for grain boundary diffusion of C is 66% of that of the energy for volume diffusion of this component.

(3) Based on prior research a vacancy mechanism is assumed to be operative for the lattice transport of C. Crystallographic considerations suggest that the lowest energy process involves an initial jump to a vacant tetrahedral site succeeded by a jump to a normally occupied C vacancy.

References

1. S. PROCHAZKA, Proceedings of the Conference on Ceramics for High Performance Applications, Hyannis, Mass. 1973, edited by J. J. Burke, A. E. Gorum and R. N. Katz (Brook Hill Pub. Co., Boston, 1975) p. 220.
2. J. A. COPPOLA and C. H. McMURTRY, presented at the American Chemical Society Symposium, "Ceramics in the Service of Man", Washington, D. C., 1976.
3. R. N. GHOSHTAGORE and R. L. COBLE, *Phys. Rev.* 143 (1966) 623.
4. J. D. HONG, Ph. D. Thesis, North Carolina State University (1978).
5. J. D. HONG and R. F. DAVIS, paper submitted for publication.
6. Y. A. VODAKOV and E. N. MOKHOV, "Silicon Carbide, 1973", edited by R. C. Marshall, J. W. Faust Jr and C. E. Ryan (University of South Carolina Press, Columbia, S. C., 1974) p. 508.
7. A. H. G. DEMESQUITE, *Acta Cryst.* 23 (1967) 610.
8. J. W. FAUST, Jr., "Silicon Carbide," edited by J. R. O'Connor and J. Smiltens (Pergamon Press, New York, 1960) p. 403.
9. V. J. JENNINGS, *Mater. Res. Bull.* 4 (1969) 5199.
10. P. T. B. SHAFFER, *J. Appl. Phys.* 39 (1968) 5332.
11. J. D. HONG and R. F. DAVIS, *Mater. Sci. and Eng.* 33 (1978) 145.
12. R. F. DAVIS, J. H. HONG and M. HON, "Processing of Crystalline Ceramics", edited by H. Palmour III, R. F. Davis and T. M. Hare (Plenum Press, New York, 1978.)
13. J. D. HONG, W. E. GRIFFIN and R. F. DAVIS, *Rev. of Sci. Instruments* 49 (1978) 83.
14. J. C. FISHER, *J. Appl. Phys.* 22 (1951) 74.
15. T. SUZUOKA, *J. Phys. Soc. Japan,* 19 (1964) 839.
16. H. S. LEVINE and C. J. MacCALLUM, *J. Appl. Phys.* 31 (1960) 3.
17. P. G. SHEWMON, "Diffusion in Solids" (McGraw-Hill, New York, 1963).
18. S. M. SZE and L. Y. WEI, *Phys. Rev.* 124 (1961) 1.
19. T. S. LUNDY and J. I. FEDERER, *Trans. Met. Soc. of AIME* 224 (1962) 12.
20. B. B. YU and R. F. DAVIS, *Phys. Stat. Sol. (a)* 51 (1979) 261.
21. M. H. HON, Ph. D. Thesis, North Carolina State University (1978).
22. T. S. LUNDY and R. A. PADGETT, *Trans. Met. Soc. of AIME* 242 (1968) 1897.
23. R. N. GHOSHTAGORE, Ph. D. Thesis, Massachusetts Institute of Techology (1965).
24. R. W. BALLUFFI and A. L. RUOFF, *J. Appl. Phys.* 34 (1963) 1634.
25. S. SARIAN and J. M. CRISCIONE, *ibid.* 38 (1967) 1794.
26. M. H. HON, R. F. DAVIS and D. E. NEWBURY, to be published.
27. D. K. DAWSON, L. W. BARR and R. A. PITT-PLADDY, *Brit. J. App. Phys.* 17 (1966) 657.
28. H. H. WOODBURY and G. W. LUDWIG, *Phys. Rev.* 127 (1961) 1083.
29. G. E. G. HARDEMAN, *J. Phys. Chem. Solids* 24 (1963) 1223.
30. W. J. CHOYKE and L. PATRICK, *Phys. Rev. B.* 2 (1970) 4959.

31. S. YAMADA and H. KUWABARA, "Silicon Carbide – 1973" edited by R. C. Marshall, J. W. Faust, Jr and C. E. Ryan (University of South Carolina Press, Columbia, S. C., 1974) p. 305.
32. S. H. HAGEN and A. W. C. VANKEMENDE, *Phys. Stat. Sol. (a).* **33** (1976) 97.
33. G. J. DIENES, *J. Appl. Phys.* **23** (1952) 11.
34. L. PAULING, "The Chemical Bond" 3rd edn. (Cornell University Press, Ithaca, New York, 1960).
35. R. C. GIFKINS, *Mat. Sci. Eng.* **2** (1967) 181.
36. C. ZENER, "Imperfections in Nearly Perfect Crystals", edited by W. Shockley (J. Wiley and Sons, New York, 1952) p. 289.