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Self-diffusion of ^{30}Si in polycrystalline β-SiC

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The ^{30}Si lattice self-diffusion coefficients in high-purity β-SiC are reported for the temperature range 2283 to 2547 K and may be represented by the expression

$$D^*_{\text{Si}} = (8.36 \pm 1.99) \times 10^7 \exp\left[\frac{(9.45 \pm 0.05\ \text{eV atom}^{-1})}{kT}\right]\ \text{cm}^2\ \text{sec}^{-1}.$$

Decomposition of the sample at the grain boundaries prevented detection of diffusion along these paths of fast transport. Lattice diffusion of Si was concluded to occur by a mechanism involving a direct jump to the nearest Si vacancy without the previous occupation of a normally unfilled position. A comparison of C and Si diffusion in this material is also given.

1. Introduction

The modern day necessity for efficient, stationary and vehicular energy conversion machines and high-temperature abrasion and corrosion-resistant materials coupled with sufficient monetary stimulation and the resulting development by Prochazka [1] and Coppola and McMurtry [2] of essentially theoretically dense β- and α-SiC, respectively, have generated a renewed consideration of these materials for previously unthinkable applications as well as a strong desire for improved knowledge of their mass-transport properties.

This report is a sequel to an earlier paper [3] concerned with the ^{14}C self-diffusion in this cubic zinc blende structure material. The summary in Table I of the Arrhenius coefficients determined from the latter effort by the Suzuoka model reveal that the diffusivity and the activation energy for ^{14}C grain-boundary transport are 10^5 to 10^6 larger (depending on T) and 33% smaller, respectively, than the analogous values for volume diffusion. It was also concluded from this research that a single vacancy mechanism, specifically, a jump to a normally occupied vacancy via a normally tetrahedral site, is the operative mechanism for C diffusion.

Although the results and discussion presented below describe the only reported Si self-diffusion study in β-SiC. Ghoshtagore and Coble [4] and more recently Hong [5] and Hong and Davis [6] have conducted somewhat similar investigations using the α form. In the former study [4], the resulting data were reported for only two temperatures and no activation energy value was calculated. In the latter investigations [5, 6] it was shown that the ^{30}Si self-diffusion coefficients are approximately two orders of magnitude lower than that of ^{14}C in the same crystal. Furthermore ^{30}Si coefficients in N-doped n-type crystals were found to be higher than in the pure α-SiC. This fact combined with the results of impurity diffusion studies strongly supports the hypothesis that Si vacancies possess acceptor character.

2. Experimental procedure

The polycrystalline β-SiC used in this research was derived from the same CVD bulk sample† as that

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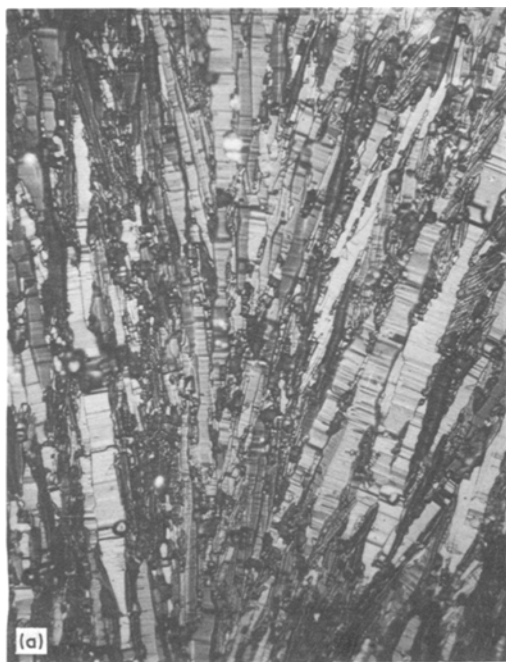
TABLE I Arrhenius coefficients for lattice (l) and grain-boundary (gb) self-diffusion of ^{14}C in CVD β-SiC determined using the Suzuoka model, from [3].

D_{0l}	Q_l (eV atom^{-1})	D_{0bg}	Q_{gb} (eV atom^{-1})
$(2.62 \pm 1.83) \times 10^8$	8.72 ± 0.14	$(4.44 \pm 2.03) \times 10^7$	5.84 ± 0.09

employed in the ^{14}C self-diffusion research and, as such, had the identical impurity, density and microstructural characteristics, as detailed in [3]. The preparation of the samples from the bulk piece was also the same.

A direct tracer deposition method similar to that descibed in the analogous work on α-SiC [5, 6] was also employed in the present research, and only the details which are cogent to the following discussion will be presented. In this deposition technique, ^{30}Si powder (95% enrichment)–acetone slurry was applied in drops to a β-SiC substrate by a camel hair brush, the acetone evaporated and the ^{30}Si melted at 1693 K to cause wetting (and therefore the removal of the thin SiO_2 layer which is always present on SiC). Samples prepared by this simpler technique and heated at the temperatures of diffusion showed no evidence of transport into the β-SiC because of the rather rapid ($< 2.0 \times 10^3$ sec) evaporation of the ^{30}Si. Prior to the completion of this evaporation, however, the ^{30}Si dissolves a portion of the β-SiC, with the grain boundaries being acutely attacked, and redeposits this dissolved material on the sample surface as a thin layer of particles as the evaporation continually saturates the molten ^{30}Si. As such, a thin layer of SiC powder bonded to the sample is the resultant configuration. In order to get the ^{30}Si species to remain at the sample surface, it was reasoned that if the molten ^{30}Si dissolved ^{30}SiC, it could deposit this latter material on the sample accompanied by simultaneous reaction with the surface. Thus, a thick layer of ^{30}SiC powder was deposited in drops onto the ^{30}Si such that this latter material, when molten, dissolved portions of both the ^{30}SiC powder and, to a larger extent, similar material from the grain boundaries of the sample. Again a thin layer was deposited on and reacted with the sample surface but which now contained some ^{30}SiC which provided a thin film tracer source for the diffusion study. Figs. 1a and b show the etching of the individual grains and the notable grain-boundary grooving by the ^{30}Si found during short time tests at 2273 K to understand this total deposition phenomenon. This grooving allowed the ^{30}SiC deposition only at sites on the larger grains.



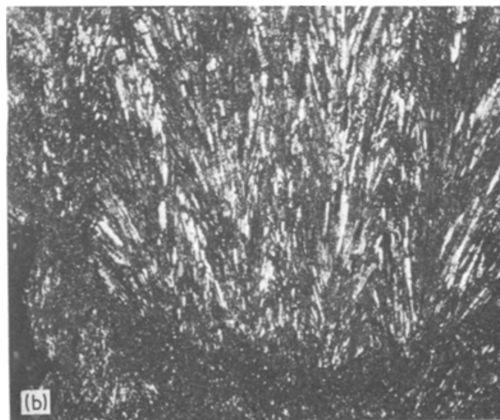


Figure 1 (a) The resultant etching of the grains and especially the boundaries by Si at 2273 K using a SiC/Si couple. The Si evaporated rapidly and left a SiC residue (not shown) which was derived from the etch (X 225). (b) The resultant etching using a SiC/Si/SiC powder sample at 2273 K. The dark regions on the left and bottom edges are SiC powder derived from the powder initially on top of the Si and a portion of which deposited as the Si evaporated. This powder originally covered the sample, but a portion was removed to reveal the etching action (X 36).

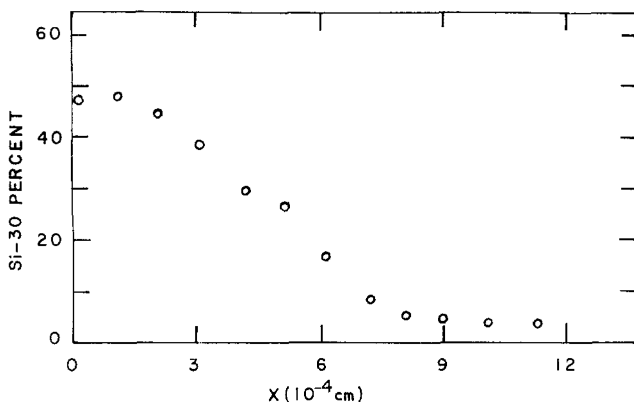


Figure 2 Representative profile of the percentage of Si concentration as a function of distance from the tracer/sample interface. The former is calculated from the raw ion microprobe data without subtraction of background.

These phenomena coupled with the very slow ^{30}Si diffusion rate prevented any true grain-boundary diffusion, as indicated by the absence of a high diffusivity, non-Gaussian tail in the diffusion profiles. The evaporation rate of ^{30}Si was mitigated to some extent by using the smallest possible ^{30}SiC-coated and sealed graphite cavity as well as placing a considerable amount of ^{30}Si in the crucible in order to produce a high ^{30}Si vapour pressure.

The combination ^{30}SiC/^{30}Si tracer/SiC samples were annealed in a graphite tube furnace in high-purity static (9×10^4 Pa) Ar in the closely monitored [7] temperature range of 2283 to 2547 K. Following the anneals, the samples were sectioned in half perpendicular to the tracer surface. The resulting end sections were polished to a 1×10^{-6} finish, mounted flat on a glass plate with a very thin layer of Duco® cement, enveloped by the drilled holes of a 1.5×10^{-2}m brass holder, fixated with epoxy casting resin and coated at the sample brass interface with Ag epoxy. The last step was necessry to prevent charge build-up during the analysis.

Ion microprobe* analysis of the ^{30}Si as a function of diffusion distance was conducted by scanning a 4×10^{-6}m diameter positively charged oxygen ion beam (18.5 keV) over the sample. A scan width of 50×10^{-6}m was employed. Initial calibration of the instrument was made by scanning a standard, natural, semiconductor grade Si sample in the same manner as the SiC sample coupled with continuous adjustment until the ^{28}Si/^{30}Si ratio was approximately 30:1 (i.e. the ratio in the natural material). The ion beam current was adjusted such that the absolute ^{30}Si count was not below 1000 in a period of 20 sec. The ion beam scan was initiated from the tracer and moved into the sample at 1×10^{-6}m steps. All the resulting ^{30}Si data obeyed well the thin-film solution to Fick's second law.

Complete details concerning the above procedures are given in [7].

3. Results and discussion

3.1. Diffusion profiles

A typical profile of the percentage of ^{30}Si concentration as a function of the distance of the centre of the ion beam from the sample/tracer interface is shown in Fig. 2. In all cases, ^{30}Si was detected prior to reaching the sample surface over a distance which, at maximum, was only 3×10^{-6}m. This presample concentration ranged from an initial amount of approximately 30% up to about 40% at the interface. The gradient was caused by the overlap of the 4×10^{-6}m beam with space containing no ^{30}Si; this volume diminished as the beam moved toward the sample. At no time was there an extended profile outside the sample, as found in the α-SiC material [5, 6].

Because of the slightly uneven sample surface produced by ^{30}Si etching during heating to and at the annealing temperature, the $x = 0$ position had to be determined with considerable care. The maximum concentration coincided closely with the edge of the sample, as determined by microscopic examination (deviation $\pm 1 \times 10^{-6}$m) and taken to be $x = 0$. Following this determination, the percentage of ^{30}Si in the background was subtracted from the percentage determined from the reworked ion probe data, such as that shown in Fig. 2, and this difference plotted on a logarithmic scale as a function of distance into the sample, as shown for several temperatures in Fig. 3. In every

*Ion Microprobe Mass Analyser (IMMA), Applied Research Laboratory, Sunland, California, USA.

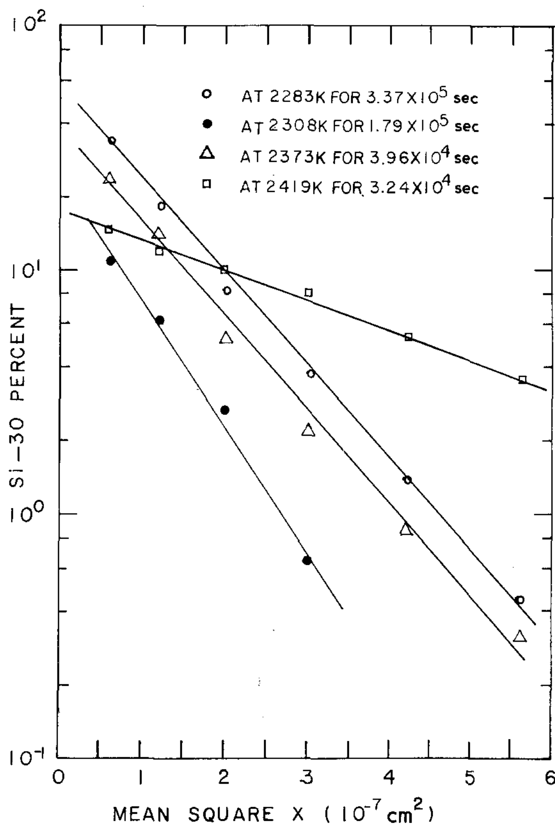


Figure 3 Representative profiles of the percentage of ^{30}Si concentration obtained by the subtraction of the background values from those in Fig. 2 as a function of the square of the distance from the tracer/sample interface.

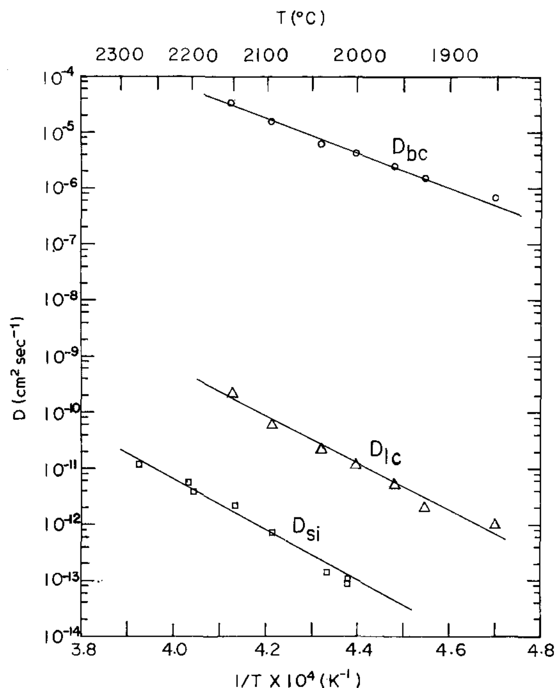


Figure 4 Self-diffusion coefficients of ^{14}C lattice and grain-boundary diffusion and ^{30}Si lattice diffusion in β-SiC as a function of $1/T$.

sample, these graphs resulted in a linear curve indicating that the thin-film solution to Fick's second law correctly described the profiles and that the tracer was derived from a true thin-film source. Silicon-30 self diffusion coefficients, subsequently calculated from the curves represented in Fig. 3, are presented in Table II and plotted in Fig. 4 as a function of $1/T$. The resulting curve follows closely an Arrhenius relationship and therefore can be expressed as

$$D^*_{\mathrm{Si}} = (8.36 \pm 1.99) \times 10^7 \exp\left(\frac{9.45 \pm 0.05\ \mathrm{eV\ atom}^{-1}}{kT}\right)\ \mathrm{cm^2\ sec^{-1}} \quad (1)$$

The values of the pre-exponential term (D_0) and the activation energy (Q) were fitted to a least square curve; the limits on these terms are the probable errors. The absence of any indication of grain-boundary diffusion is directly related to the decomposition of the sample at the grain boundaries, as discussed in the previous section. This coupled with the closeness of fit to the thin-film solution strongly indicates that the diffusion profiles contain no grain-boundary contribution.

TABLE II Diffusion coefficients of ^{30}Si in polycrystalline β-SiC

Sample number	T(K)	$1/T$ (1/K) $\times 10^4$	t (sec)	D (cm^2 sec^{-1})
C-2a	2283	4.38	3.37×10^5	$(8.66 \pm 0.21) \times 10^{-14}$
C-2b	2283	4.38	3.37×10^5	$(1.01 \pm 0.02) \times 10^{-13}$
C-8	2308	4.33	1.79×10^5	$(1.39 \pm 0.05) \times 10^{-13}$
A-3a	2373	4.21	4.77×10^4	$(1.89 \pm 0.06) \times 10^{-12}$
D-5	2419	4.13	3.24×10^4	$(2.22 \pm 0.23) \times 10^{-12}$
D-4	2473	4.04	1.08×10^4	$(3.92 \pm 0.17) \times 10^{-12}$
B-6	2480	4.03	1.08×10^4	$(5.82 \pm 0.25) \times 10^{-12}$
B-3	2547	3.93	6.0×10^3	$(1.20 \pm 0.03) \times 10^{-11}$

TABLE III Data on decomposition of bulk pieces of polycrystalline CVD-produced β-SiC

Sample number	Annealing temperature (K)	Annealing time (sec)	Decomposition thickness $Vt \times 10^6$ (m)	Decomposition rate V (cm sec^{-1})	$R = V\rho \times 10^3$ (mg cm^{-2} sec^{-1})
B-605	2128	5.08×10^5	0.40	7.87×10^{-11}	2.53×10^{-7}
B-608	2260	2.62×10^5	1.82	7.0×10^{-10}	2.25×10^{-6}
B-310	2260	2.62×10^5	1.98	7.5×10^{-10}	2.41×10^{-6}
B-610	2391	1.11×10^4	0.91	8.20×10^{-9}	2.63×10^{-5}
B-606	2423	1.13×10^4	0.77	6.81×10^{-9}	2.19×10^{-5}
B-312	2448	2.76×10^3	0.72	2.61×10^{-8}	8.39×10^{-5}

Grain growth was not observed to occur during the diffusion anneals.

It is also important to determine experimentally whether decomposition creates errors in the concentration and the values of D_{Si} as a function of temperature and/or Q which are outside the calculated experimental errors in these parameters. As such, the decomposition rate of the CVD β-SiC used in this research was determined on samples analogous to and subjected to the same environmental conditions as those used in both the C [7] and the Si diffusion experiments. As the configuration in both types of determinations consisted of one sample of β-SiC on top of a similar or tracer material [7], both the rate of movement of the surface position (V) and the rate of weight loss per unit area (R) were determined from the top sample. The resulting data and calculations are presented in Table III and Fig. 5, respectively.

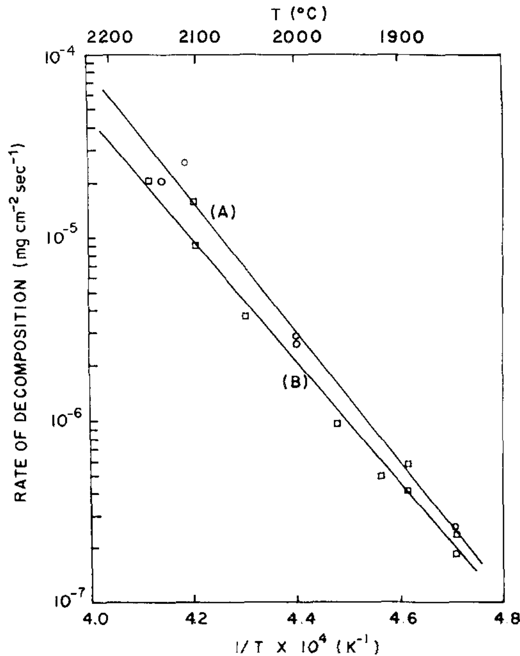


Figure 5 Rate of decomposition of α- and β-SiC as a function of $1/T$.

The individual values of V were calculated by dividing the weight loss of each of the top samples by the density of β-SiC ($= 3.213 \times 10^3$ kg m^{-3}), the surface area and the annealing time; collectively, they are described by the equation:

$$V = 2.41 \times 10^7 \exp\left(\frac{-07.40 \pm 1.20 \text{ eV atom}^{-1}}{KT}\right) \text{cm}^2 \text{ sec}^{-1} \quad (2)$$

If the density of β-SiC is multiplied by the values of V, the values of R can be calculated; an equation of the curve of these latter numbers was determined to be

$$R = 7.74 \times 10^{10} \exp\left(\frac{-7.40 \pm 1.20 \text{ eV atom}^{-1}}{kT}\right) \text{mg cm}^{-2} \text{ sec}^{-1}. \quad (3)$$

Fig. 5 also provides a comparison between the decomposition of α-SiC single crystals under the same environmental conditions as reported by Hong and described by the equation

$$R = 2.95 \times 10^8 \exp\left(\frac{-6.29 \pm 0.09 \text{ eV atom}^{-1}}{kT}\right) \text{mg cm}^{-2} \text{ sec}^{-1}, \quad (4)$$

and the bulk polycrystalline β-samples employed in this study. The decomposition rate of the former is very slightly lower than the latter, which confirms similar results of Shaffer [8] on powders of these two materials. The principal reason for the measurable decomposition differences in the α and β samples in the present case is the presence of the large amount of grain-boundary interfacial area which facilitates decomposition, particularly at the higher temperatures, from a number of sites rather than from just the top surface layer, as in the single crystal case.

Dawson *et al.* [9] have studied the effect of evaporation of the sample surface on self-diffusion

of Br in KBr and found that as long as the ratio $Vt/(Dt)^{1/2} \leqslant 0.04$, the diffusion coefficient, D, will not be in error by more than 5% if sample evaporation is neglected.

In the case of diffusion experiments from a thin film into materials which are either evaporating or dissociating at a velocity comparable to but less than that of diffusion, it is still possible to obtain Fickian concentration profiles at deep penetrations. An analytical solution, Equation 5, has been derived for this case by Ghoshtagore [10] using the assumption that $Vt \leqslant (Dt)^{1/2}$.

$$C(x', t) = Q \left\{ \frac{e - [(x' + Vt)/2\,(Dt)^{1/2}]^2}{(\pi Dt)^{1/2}} - \frac{V}{2D} \operatorname{erfc}\left[\frac{x' + Vt}{2\,(Dt)^{1/2}}\right] \right\}, \quad (5)$$

where C is the concentration at x' at any time, t; x' is a reference co-ordinate inside the diffusion profile in the sample which allows the measurement of the changing surface position; Q is the total amount of tracer species in the infinitesimally thin-film; V is the rate of movement of the boundary and D is the diffusion coefficient. This author [10] has given an example of the use of Equation 5 in the limiting case where $Vt/(Dt)^{1/2} = 1$ and showed that the calculated value of D was 20% lower than the assumed value.

In the present study, the $Vt/(Dt)^{1/2}$ ratio was calculated to be approximately 0.9; thus, the decomposition will play some role in determining the diffusion coefficients. Unfortunately the use of Equation 5 in ascertaining this effect of D_{Si} is not possible in the present case as only a percentage of the ^{30}Si was obtained and not the value of the total amount. Therefore, the values of Q are not known. Furthermore, the diffusion distance of the ^{30}Si is short; thus, there are no deep portions which could, with confidence, be considered to be only negligibly affected by the decomposition and therefore amenable to extrapolation to $X \to 0$ for comparison with the actual curve and the calculation of D in the affected region. The values of D and V are, however, similar to those used by Ghoshtagore in his example; thus, the ^{30}Si diffusion coefficients may be up to 20% lower, as a worst case, than the real values. However, since the ratios of $Vt/(Dt)^{1/2}$ were nearly constant in the temperature range of this study, the calculated activation energy should not be affected.

3.2. Crystallographic mechanisms of diffusion

The arguments presented in the companion paper on ^{14}C diffusion in β-SiC also provide support for the assumption that Si diffuses by a vacancy mechanism. Choyke and Patrick [11] have observed a N donor–Al acceptor pair spectra which is in agreement with the Al occupation of the Si sites. Vodakov and Mokhov [12], in their review of the transport of Al and Ga in α-SiC, have reported that these dopants diffuse via Si vacancies. Initial work by Ghoshtagore and Coble [4] and a much more extensive effort by Hong and Davis [6] concerning the diffusion of Si in α-SiC have also shown that transport of this component by a vacancy mechanism is the most logical mode, given the high, single valued, experimentally determined activation energy value of 7.8 eV. Theoretical considerations are also of value in this matter. The diffusion activation energy for a vacancy mechanism consists of the energies of vacancy formation and vacancy migration. As shown in [3], the energy required to form a vacancy, ΔH_f, in SiC is estimated to be 6.0 eV atom^{-1}. This should be approximately true for both α- and β-SiC; since, the densities are essentially equal and the bond strengths should be approximately the same despite the differences in crystallographic structure and atomic stacking sequence. Therefore, the difference in the diffusion energies of Si in α- and β-SiC ($9.45 - 7.8 = 1.65$ eV atom^{-1}) would be equivalent to the difference in vacancy migration energies. The sequences of atomic stacking in the various polytypes of this material do affect the diffusion paths, as shown in [3] and [5] and in the discussion presented below. In turn, these different avenues of transport require different amounts of energy for atomic dilation to allow the diffusing atom to move to an unfilled site. Thus, from the above considerations, it is concluded that the vacancy mechanism is also relevant for Si transport in β-SiC.

The crystal structure of β-SiC is that of zinc blende shown in Fig. 6 where the Si positions are at 000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$ and C is at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ plus each Si position. From a consideration of the radii of the unfilled tetrahedral (0.8 Å) and octahedral (1.01 Å) sites and the covalent radius of Si (1.17 Å), it is reasonable to assume that Si could, if necessary, only occupy the octahedral sites without considerable lattice distortion. As such, two transport paths are thought to be the

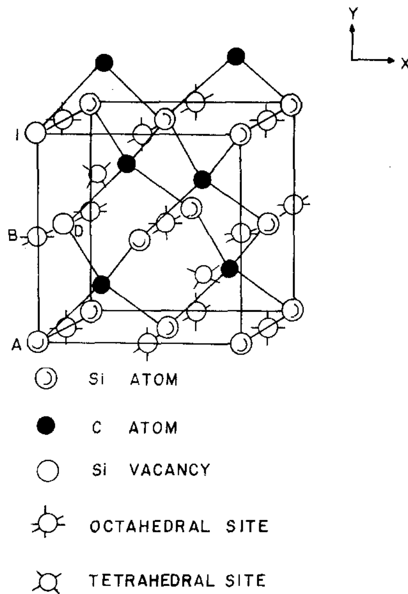


Figure 6 Beta-SiC unit cell for illustrating the possible paths of Si diffusion.

most feasible for movement of this species from one plane to another along an arbitrarily assigned y direction. Choosing, for example, the atom labelled A in Fig. 6, the two paths are A, D, I, . . . and A, B, I, . . . , respectively. The first path is a single jump which necessitates the presence of a Si vacancy at D and the dilation of 2 to 3 Si atoms in order to occupy the vacancy. The second path requires the initial dilation of 4 to 5 Si atoms to move into the octahedral site at B, the presence of a Si vacancy at I and the dilation of four additional Si atoms around I. In the latter movement, the moving Si atom would also encounter considerable electrostatic repulsion from the Si atoms around the octahedral position. Lateral movement from the octahedral site is also possible; however, dilation of four additional Si atoms and the repulsion in the octahedral space must still be overcome. If movement in the negative y direction is not considered, a Si atom has four equivalent positions to which to jump if transport is directly to a Si vacancy but five equivalent positions if the octahedral site is used. Thus, the probability of finding a vacancy is greater in the latter. Nevertheless, a synthesis of the above information and the fact than only one activation energy is found in the temperature range employed leads the authors to the hypothesis that Si moves directly to a vacant position along the lower energy paths analogous to A, D, I, ...

3.3. Comparison of C and Si diffusion

From Fig. 4, it may be immediately determined that the lattice self-diffusion of ^{14}C is more rapid than that of ^{30}Si. This is in agreement with the theory of Tomonari [13] from his study of the kinetics of SiC formation and the results of Hong [5] in a similar study in α-SiC single crystals.

The reason for the approximately two orders of magnitude larger ^{14}C diffusivity is incorporated primarily in the factors which compose the activation energy. The exponential activation energy term for C is more than 30 times larger than that for Si while the D_0 term for C is only about 3 times greater.

The values of D_0 obtained for both species are quite high; however, as discussed in [3], the value of D_0 is exponentially proportional to the value of ΔS in which is incorporated the entropies of vacancy formation and atom migration. Furthermore, from the Zener theory [14], ΔS is proportional to the energy of migration which, in SiC, is deemed to be quite high. It should be noted that similar (and higher) values of D_0 have also been obtained in self-diffusion studies in other compound semiconductors [15–17].

Van Vechten [18] has shown that the single vacancy formation energy in compound semiconductors is composed of both short-range and long-range energies. For a compound such as SiC, the short-range or broken bond contribution is the same for both C and Si. The difference between these two species is derived only from the long-range contribution, which is proportional to square of the atomic radius (r). Thus, Si with the larger r (1.17 Å), should have a larger vacancy formation energy than C (0.77 Å) and therefore a larger diffusion activation energy.

4. Conclusions

(1) The ^{30}Si lattice self-diffusion coefficients in β-SiC for the temperature range 2283 to 2547 K can be expressed as

$$D^*_{Si} = (8.36 \pm 1.99) \times 10^7 \times \exp\left[\frac{(9.45 \pm 0.05\,\text{eV atom}^{-1})}{kT}\right] \text{cm}^2\,\text{sec}^{-1}.$$

Grain-boundary diffusion of Si was not detected because of the decomposition of the sample and the subsequent evaporation of the tracer at the boundaries.

(2) A vacancy mechanism is concluded to be

operative for the self-diffusion of Si. The lowest energy migration route is believed to be the direct jump to the nearest Si vacancy without the occupation of an intermediate vacant octahedral position.

(3) Carbon is the faster diffusing component in the lattice of β-SiC. This difference is approximately two orders of magnitude in the temperature range of this study and is caused principally by the factors which compose the activation energy term.

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