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Self-diffusion of silicon-30 in α-SiC single crystals

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The self-diffusion of ^{30}Si in high purity and N-doped α-SiC single crystals has been measured in the temperature range 2273 to 2573 K. The diffusion (D^*_{Si}) in N-doped crystals exceeds that in the pure crystals because of the increase in the concentration of the charged acceptor-type Si vacancies in the presence of the N species. A comparison of D^*_{C} and D^*_{Si} shows that the former exceeds the latter by approximately 10^2, primarily because of the greater entropy of migration of C. Possible crystallographic paths of transport for both species are also discussed.

1. Introduction

High temperature technology continually requires an extremely strong, high melting point material which is resistant to rapid oxidation, corrosion, creep and fracture via thermal shock. SiC has long been a candidate material for use in these environments and with the development of the essentially theoretically dense polycrystalline β- and α-SiC by Prochazka [1, 2] and Coppola and McMurtry [3] a renewed interest in this material has been generated for a variety of applications in which atomic mass transport may play an important role in property determination.

An earlier paper [4] by the present authors showed that ^{14}C self-diffusion in high purity α-SiC is faster than in the analogous N-doped crystals in the temperature range 2123 to 2453 K. The equations which describe this transport are

$$D^*_{\text{C}} = (8.62 \pm 2.01) \times 10^5 \times \exp\left(-\frac{7.41 \pm 0.05\,\text{eV atom}^{-1}}{kT}\right) \text{cm}^2\,\text{sec}^{-1}\ \text{(pure)} \quad (1)$$

$$D^*_{\text{C}} = (3.32 \pm 1.43) \times 10^7 \times \exp\left(-\frac{8.20 \pm 0.08\,\text{eV atom}^{-1}}{kT}\right) \text{cm}^2\,\text{sec}^{-1}\ \text{(N-doped)} \quad (2)$$

where D^*_{C} is the diffusion coefficient of C. The reason for the difference in the coefficients is the decrease in the solubility of the donor-type charged C vacancies and therefore the total number of vacancies caused by the presence of the donor N impurity atoms. This in turn lowers the probability of the presence of a C vacancy in which to accomodate the transport of this species through the crystal.

In the only analogous research, Ghostagore and Coble [5] have reported ^{30}Si self-diffusion data in Al-doped (600 ppm) single crystals for two temperatures, however, because of the considerable scatter, no activation energy was calculated. Furthermore, the Si diffusion coefficients were reported to be considerably larger than those for C, in contrast to that found in the present study reported below.

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2. Experimental procedure

2.1. Tracer (^{30}Si) deposition

The α-SiC single crystals† employed in this research were identical in source, polytype(s) and impurity level. They were from the same populations as those used in the C self-diffusion studies reported earlier [4], i.e. (a) high purity, essentially electronically intrinsic and (b) N-doped ($\simeq 3 \times 10^{25}$ atoms m^{-3} = 620 ppm), n-type materials. The sample preparation procedures were identical to those reported earlier up to the point of tracer deposition.

It was initially reasoned that the existence of the 3.1 at % of ^{30}Si in the natural Si of SiC would require an amount of ^{30}Si tracer in excess of that provided by a thin film. Although this was much later discovered to be unnecessary, an infinite source method using a highly enriched ^{30}Si tracer was deemed the most feasible technique from both an experimental and mathematical point of view. The initial attempt to deposit a thick ($\simeq 50 \times 10^{-6}$ m) tracer layer of ^{30}SiC on the crystal involved the use of the traveling solvent method (TSM) employed in the C self-diffusion study [4]. However, the higher (2073 K) temperature necessary for this greater amount of deposition produced (1) a faster reaction of the yttrium with the tracer as well as the seed crystal, (2) a greater solubility of SiC in the Y, and (3) a subsequent deposition of a mixture of ^{30}Si and ^{28}Si which formed an increasing ratio across the crystal–layer interface over a distance of about 10×10^{-6} m, rather than a more analytically feasible discontinuous jump in ^{30}Si concentration at this interface. Thus, a purely "infinite" source was not produced and the resulting diffusion could not be analysed with complete confidence in terms of accuracy. The results of this effort are reported by Davis *et al.* [6].

Several additional experiments were conducted and also quantitatively analysed with the ion microprobe to determine the most suitable method to produce an "infinite" source. The results of these tests revealed that a ^{30}Si–^{30}SiC combination produced profiles which mathematically fit the solution for diffusion from this type of tracer source. A ^{30}Si‡ powder (95% enrichment) was mixed in chemically pure acetone to form a slurry which was evenly applied to one surface of an optically smooth crystal as a small droplet formed on the end of a very fine camel hair brush. Upon evaporation of the acetone, the crystal–^{30}Si combination was placed in the shallow cavity of a graphite boat, positioned in a thermal evaporator and heated in vacuum to $\simeq 1693$ K to melt the ^{30}Si and to cause wetting of the crystals (and therefore removal of the thin SiO_2 layer which is always present on SiC). Samples prepared by this method and annealed at 2273 K showed evidence of diffusion, in contrast to the total absence of transport in the β-SiC materials [7]. Evaporation of the ^{30}Si also occurred; however, unlike that found in the polycrystalline β material, reaction with the single crystals of α was very slow and the amount of SiC deposited during the evaporation of the Si was relatively very small. In order to more effectively retain and bond the tracer on the surface of the crystals, 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, the premelted ^{30}Si was heavily coated with a ^{30}SiC powder§–acetone slurry in the same manner as the ^{30}Si. The resulting ^{30}SiC–^{30}Si–SiC crystal samples were placed in a vacuum tight graphite¶ inner crucible having a tapered cap with an external hemispherical head and held in place by a threaded cap (also with a rounded head) which was a cover for an outer graphite¶ crucible. The evaporation of ^{30}Si was mitigated to some extent by surrounding (without direct contact) the samples with 0.5×10^{-6} kg of ^{30}Si. The very small volume of the inner crucible and the double coating of its inside walls with ^{30}SiC also assisted this mitigation.

The heating, cooling and argon atmospheric procedures and conditions used in the C self-diffusion research were also employed for this study except for the higher temperature range (2273 to 2573 K) necessary for diffusion.

As only a small amount of dissolution of the α-

†The crystals were obtained from J. M. Blank and R. M. Potter, General Electric Company, Lighting Research Laboratory, Nela Park, Ohio. All crystals were grown under identical conditions except for the N-doping.

‡Isotope Sales Department, Oak Ridge National Laboratory, Oak Ridge, Tennessee. The powder of this isotope also contains (in wt%) ^{28}Si: 3.78, ^{29}Si: 0.67, Na: 0.1, B: < 0.1, Ba: < 0.1, K: < 0.1.

§This powder was prepared in the same manner as described for for the $Si^{14}C$ material [4].

¶Type DFP-3, Poco Graphite Inc., Decatur, Texas 76234, USA.

crystals by the ^{30}Si occurs, the metal is principally saturated by the ^{30}SiC powder. Thus, during evaporation, a thick layer containing a high percentage of ^{30}SiC is deposited on and chemically bonded with the crystals to form the infinite source of tracer. It should be noted that no diffusion profiles emanate from the sides or the bottom of the crystal. It is thus surmised that ^{30}Si vapour does not contribute to the diffusion in these materials.

2.2. Tracer profile analysis

After diffusion annealing, the samples were cut in half perpendicular to the tracer surface. The two resulting sections (approximately 2×10^{-3} m by 1×10^{-3} m) were polished to a 1×10^{-6} m finish, mounted flat on a glass plate with a very thin layer of Duco^T cement, enveloped by the small holes drilled in a 1.5×10^{-2} m diameter by 0.5×10^{-2} m brass holder, fixated with epoxy casting resin and coated at two sample–brass interfaces with Ag epoxy by heating to 373 K for 2 h to ensure conduction between the samples and the brass holder. The last process was necessary to prevent charge buildup 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. The profile penetration distance was established by the centre of the ion beam and the profile shape determined by moving the beam from the tracer into the crystal in 1×10^{-6} m steps. Initial calibration of the instrument was made by scanning a standard semiconductor grade Si sample in the same manner as the SiC samples, 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 2000 in a period of 20 sec (sample current of 1 to 3×10^{-9} Å). The centre region of the sample was chosen as the scan area to eliminate any possibility of a contribution to the ^{30}Si counts from the surface diffusion.

2.3. Infinite composite medium solution

In general, two extended mediums are present. Experimentally, medium I at $x > 0$ (e.g. the applied tracer meterial) containing some isotropic species (e.g. ^{30}Si) in which the diffusion coefficient is D_1 and medium II at $x < 0$ (e.g. the specimen) in which the diffusion coefficient of the same isotropic species is D_2 are joined at the plane $x = 0$. If the initial conditions are

$$C = C_0 \qquad \text{for } x > 0, t = 0 \qquad (3)$$

$$C = 0 \qquad \text{for } x < 0, t = 0 \qquad (4)$$

and the boundary conditions are

$$C_2/C_1 = K \qquad \text{at } x = 0, t > 0 \qquad (5)$$

$$D_1 \frac{\partial C_1}{\partial x} = D_2 \frac{\partial C_2}{\partial x} \qquad \text{at } x = 0, t > 0 \qquad (6)$$

where C_1 and C_2 are the concentrations of the diffusing species in mediums I and II, respectively, and K is the ratio of the uniform concentration of this species in medium II to that in medium I. When final equilibrium is achieved, then the solutions to this problem can be expressed as [8]

$$C_1 = \frac{C_0}{1 + K(D_2/D_1)^{\frac{1}{2}}} \times \left[1 + K(D_2/D_1)^{\frac{1}{2}} \operatorname{erf} \frac{x}{2(D_1 t)^{\frac{1}{2}}}\right] \qquad (7)$$

$$C_2 = \frac{KC_0}{1 + K(D_2/D_1)^{\frac{1}{2}}} \operatorname{erfc} \frac{|x|}{2(D_2 t)^{\frac{1}{2}}}. \qquad (8)$$

For the Si study in this research, only the diffusion in medium II is of interest. Noting that K, C_0, D_2, D_1 in Equation 8 are constant for each diffusion experiment and setting $S = KC_0/[1 + K(D_2/D_1)]$ at $x = 0$ and $t > 0$, $C_2(0, t) = S$. Thus, Equation 8 becomes

$$C_2(x, t) = S \operatorname{erfc} \frac{|x|}{2(D^2 t)^{\frac{1}{2}}}$$

$$= C_2(0, t) \operatorname{erfc} \frac{|x|}{2(D_2 t)^{\frac{1}{2}}} \qquad (9)$$

If the initial conditions change to

$$C = C_0 \qquad \text{for } x > 0, t = 0 \qquad (10)$$

$$C = C_0' \qquad \text{for } x < 0, t = 0 \qquad (11)$$

then the solution corresponding to Equation 9 will be

$$C_2 - C_0' = [C_2(0, t) - C_0'] \operatorname{erfc} \frac{|x|}{2(D_2 t)^{\frac{1}{2}}}.$$

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

In determining the diffusion coefficient from Equation 12, one may initially calculate the ratio $(C_2 - C_0')/(C_2(0, t) - C_0')$ for a given x. From this value, the quantity $x/2(D_2 t)^{1/2}$, and therefore D_2, may be obtained from tabulated values of the error function. However, Malkovich [9] has presented another method which permits one to obtain more reliable quantitative values of the diffusion coefficients. In this method, the logarithm of the derivative of Equation 12 with respect to x results in an equation of the form

$$\ln\left(-\frac{\mathrm{d}C_\mathrm{P}}{\mathrm{d}x}\right) = \ln\frac{C_\mathrm{q}}{(\pi D_2 t)^{\frac{1}{2}}} - \frac{x^2}{4D_2 t} \quad (13)$$

where $C_\mathrm{p} = C_2 - C_0'$ and $C_\mathrm{q} = C_2(0, t) - C_0'$. Thus, a plot of $\ln(-\mathrm{d}C_\mathrm{p}/\mathrm{d}x)$ against x^2 should result in a straight line whose slope is equal to

$$D_2 = -\frac{1}{4t}\left[\frac{1}{\frac{\mathrm{d}}{\mathrm{d}(x^2)}\ln -\frac{\mathrm{d}C_\mathrm{p}}{\mathrm{d}x}}\right]. \quad (14)$$

In practice, D_2 can be accurately determined if one takes a very small $(1 \times 10^{-6}$ m) section for each corresponding position and couples this with the use of the approximation

$$\left.\frac{\mathrm{d}C_\mathrm{p}}{\mathrm{d}x}\right|_{x = x_0} \simeq \frac{C_{\mathrm{P}_1} - C_{\mathrm{P}_2}}{x_1 - x_2} = \frac{\Delta C_\mathrm{P}}{\Delta x}\; x = x_0 \quad (15)$$

(where x_0 is the midpoint between x_1 and x_2) within this small section. Thus, Equation 14 becomes

$$D_2 = -\frac{1}{4t}\left|\frac{1}{\frac{\mathrm{d}}{\mathrm{d}(x^2)}\ln \frac{-\Delta C_\mathrm{p}}{\Delta x}}\right|. \quad (16)$$

In the present study, the thickness of the residual ^{30}Si tracer following the diffusion anneals was always at least 30×10^{-3} m. This thickness considerably surpassed the measured diffusion depths of $\simeq 1 \times 10^{-6}$ m and thus satisfied the boundary conditions for the "infinite" source solution, Equation 9. However, the Si of the SiC crystals also contains a natural abundance of 3.09 at % ^{30}Si, and the diffusion profiles were determined at every 1×10^{-6} m in the diffusion region. As such the concentration change in this one micron region was assumed linear within experimental error; thus, Equation 16 was appropriate for the analysis of the ^{30}Si diffusion profile for this research.

Complete details concerning the above procedures are given by Hong [10].

3. Results and discussion

3.1. Diffusion data

Fig. 1 shows a ^{30}Si concentration profile which is representative of both the high purity, essentially intrinsic and N-doped, n-type α-SiC single crystals for diffusion along the ⟨0001⟩ direction. This figure was produced by plotting the ^{30}Si enrichment, calculated from the total counts of ^{30}Si and ^{28}Si using the equation

$$^{30}\mathrm{Si}(\%) = \frac{^{30}\mathrm{Si}/^{28}\mathrm{Si}}{1 + {}^{30}\mathrm{Si}/^{28}\mathrm{Si}} \times 100 = \frac{^{30}\mathrm{Si}}{^{30}\mathrm{Si} + {}^{28}\mathrm{Si}} \times 100 \quad (17)$$

versus the penetration distance at each position. ^{30}Si and ^{28}Si are the intensities measured by the ion microprobe at each point along the profile. In this case, the presence of the 3.09% natural abundance of ^{30}Si is advantageous, as the microprobe can analyse the ^{30}Si/^{28}Si ratio without concern for the correctness of the absolute value of either individual species. It should be noted that the isotope intensity of ^{29}Si falls within the limits of experimental error ($\simeq$ 4%) and is thus neglected.

As the ^{30}Si concentration profile was determined by moving the beam from the tracer into the crystal, the interface position along the profile must be determined. Therefore plots of the concentration gradient calculated from the difference in ^{30}Si enrichment per unit length $(1 \times 10^{-6}$ m) against the penetration distance for each sample were also produced in order to determine the tracer–crystal interface position ($x = 0$) in the profile (i.e. the position at which the absolute value of the concentration gradient is a maximum) as shown by the derivative of Equation 12 with respect to x. Fig. 1b shows a typical concentration gradient curve as derived from Fig. 1a. Plots of the logarithm of the concentration gradient from $x = 0$ into the crystals against the square of the penetration distance at each point such as that shown in Fig. 2 resulted in a straight line having a slope equal to $1/(4Dt)$ for every sample. This is another indication that the use of an "infinite" source solution is indeed correct. Furthermore, because of the use of the "infinite" ^{30}SiC source layer, the decomposition of the tracer surface did not influence the diffusion region, i.e. the interface position did not change during the diffusion annealing. Thus, no decomposition correction was

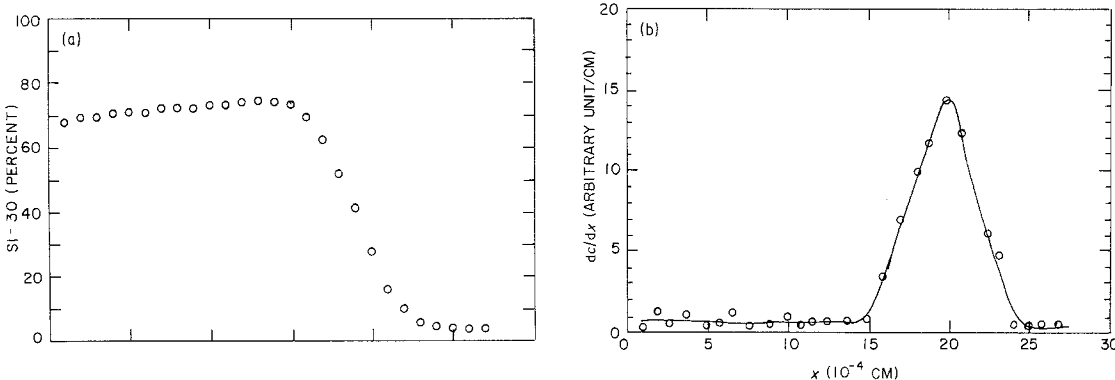

Figure 1 (a) Typical concentration profile of the percentage of ^{30}Si concentration as a function of distance for the tracer/α-SiC single crystal combination along the ⟨0001⟩ direction. The former is calculated from raw ion microprobe data without subtraction of the background. The initial portion of the data along the tracer layer is omitted for the sake of brevity, (b) typical concentration gradient of ^{30}Si against the penetration distance derived from the plot in (a) using the derivative of Equation 12 with respect to x. The maximum value of the gradient signifies the position $x = 0$.

applied to any of the calculated ^{30}Si diffusion coefficients.

^{30}Si self-diffusion coefficients calculated from the concentration gradient curves using Equation 16 are plotted in Fig. 3 as a function of $1/T$ along

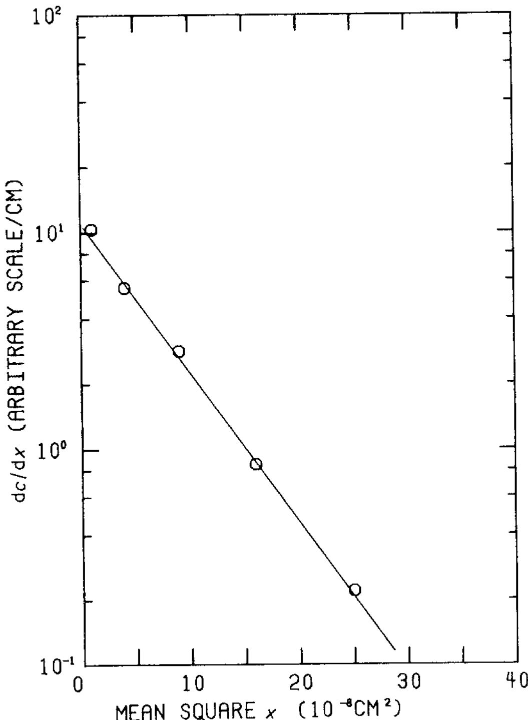

Figure 2 Concentration gradient of ^{30}Si from the maximum point shown in Fig. 1b ($x = 0$, i.e. the tracer crystal interface) into the crystal against the square of the penetration distance.

with the analogous curves from the ^{14}C diffusion research. The resulting curves for the 2273 to 2573 K temperature range can be expressed as follows:

(1) high purity, essentially intrinsic α-SiC single crystals along the ⟨0001⟩ direction

$$D^*_{\text{Si}} = (5.01 \pm 1.71) \times 10^2 \times \exp \frac{-7.22 \pm 0.07\,\text{eV atom}^{-1}}{kT} (\text{cm}^2\,\text{sec}^{-1})^\dagger (\text{pure}); \quad (18)$$

(2) for diffusion in the N-doped, n-type α-SiC single crystals along the ⟨0001⟩ direction

$$D^*_{\text{Si}} = (1.54 \pm 0.78) \times 10^5 \times \exp \frac{-8.18 \pm 0.10\,\text{eV atom}^{-1}}{kT} (\text{cm}^2\,\text{sec}^{-1}) \; (\text{N-doped}). \quad (19)$$

In both equations the values of the activation energy and the pre-exponential factor were computer-fitted to a least square curve.

From the results, it is found that Si diffuses faster in the N-doped, n-type materials than in the high purity, essentially intrinsic α-SiC single crystals, in contrast to what is observed in the ^{14}C self-diffusion study [4]. However, if one follows the reasoning presented in the ^{14}C discussion to prove the donor or acceptor character of the Si vacancy, some frustration results owing to the dearth of evidence presently available. Assumptions can be

† Although SI units are used throughout the paper, the units of cm^{2}sec^{-1} for D are still universally employed. For the sake of comparison with other data and to avoid confusion, this convention is maintained herein.

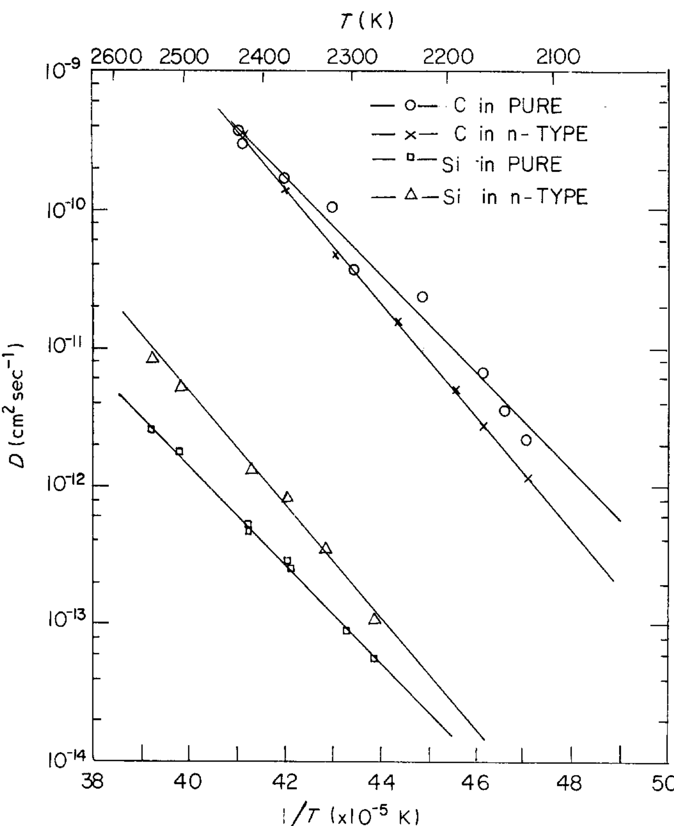

Figure 3 Self-diffusion coefficients of ^{14}C and ^{30}Si in high purity and N-doped α-SiC single crystals as a function of $1/T$.

inferred, however, from other types of investigations.

3.2. Defect interactions and diffusion of ^{30}Si

With the exception of the present research, Ghoshtagore and Coble [5] have been the only group to examine Si self-diffusion in α-SiC single crystals; however, only one crystal type was used and the results were very limited, as noted in the introduction.

Choyke and Patrick [11] have observed an N donor–Al acceptor pair spectra which is in agreement with the N on the C sites and Al on the Si sites. Although numerous investigators have studied the diffusion of Al in α-SiC, only Vodokov and Mokhov [12], in their review of Al and Ga diffusion in this material, note that these dopants diffuse through Si vacancies. These authors also indicate that a deceleration of the Al diffusion occurs during the diffusion process because of the decrease in the total concentration of Si vacancies. This is believed to indicate that the charged portion of the Si vacancies are acceptor (negatively charged in nature) and the introduction of the Al acceptor impurity decreases the number of Si vacancies because of the defect interactions noted in the discussion of C diffusion.

No effects of the presence of N or other impurities on the diffusion of Al in SiC have been reported. However, assuming that the charged portion of the Si vacancies are acceptor in character and that a vacancy mechanism is operative in the Si self-diffusion and following the defect interaction discussion given by Hong and Davis [4], the presence of the positively charged N donor atoms raises the Fermi level of the SiC crystal and its electronic free energy. Electronic equilibrium is again restored by the increase in the number (i.e. the solubility) of the acceptor-type charged Si vacancies. This increases the total number of vacancies on the Si sublattice and therefore the probability of one being available for ^{30}Si diffusion. Thus one may see that the presence of the N affects the vacancy concentrations on both sublattices in the compound semiconductor.

3.3. Comparison between D^*_C and D^*_{Si}

The most obvious characteristic of Fig. 3 is that C diffuses more rapidly than Si, in agreement with

the theory of Tomonari [13]. The reason(s) for this notable difference are primarily incorporated in the factors which produce the higher D_0 value of the C atom; since, the activation energy, Q, values of the respective high purity and N-doped samples are essentially the same for C and Si diffusion.

As noted above, previous research on self- and impurity-diffusion in α-SiC as well as the order of magnitude of the activation energies determined in this research support the assumption of a vacancy transport mechanism.

Zener [14] has developed an empirical method for calculating ΔS_m based on the elastic strain established in the lattice as an atom moves from one point to the next. This equation is given by

$$\Delta S_m = \lambda\beta \frac{\Delta H}{T_{mp}} \quad (20)$$

where λ is a constant $\simeq 0.55$, β is a constant equal to $-\mathrm{d}(\mu/\mu_0)/\mathrm{d}(T/T_{mp})$, where μ and μ_0 are the elastic shear moduli at a given temperature, T and 0 K, respectively, and T_{mp} is the melting point of the solvent (vacancies are the solute in the case of self-diffusion). This equation shows that ΔS is proportional to the activation energy of diffusion. Thus, since large values of Q were determined, the resulting large values of ΔS should also be expected.

Van Vechten [15] has treated the vacancies in group IV semiconductors as macroscopic cavities and determined that the neutral vacancy formation energy for Si should considerably exceed that for C. Since Q is composed of the energies of vacancy formation (ΔH_f) and atom migration (ΔH_m) and since the activation energies for both C and Si are similar, one may write

$$\Delta H_{fC} + \Delta H_{mC} \simeq \Delta H_{fSi} + \Delta H_{mSi}. \quad (21)$$

From Van Vechten's calculations

$$\Delta H_{fC} < \Delta H_{fSi}. \quad (22)$$

Therefore from Equation 20,

$$\Delta H_{mc} > \Delta H_{mSi}. \quad (23)$$

Since from Equation 20, $\Delta S_m \propto \Delta H_m$, and combining Equations 20 and 23 one obtains

$$\Delta S_{mC} > \Delta S_{m\,Si}. \quad (24)$$

Although accurate values of ΔS_f are not known, they are normally considered to be much less than ΔS_m, with the latter parameter being the controlling factor in the entropy term of D_0 of the diffusion equation. Therefore the greater energy of migration of the C atom produces a higher positive value of ΔS_m for C than for Si which, in turn, produces both a higher value of the pre-exponential term and, therefore, a higher diffusion coefficient for the former species.

The crystal structure of α-SiC is, in essence, a hexagonal closest-packed array of Si atoms with the smaller C atoms occupying one half of the tetrahedral sites. The remaining octahedral and tetrahedral voids may now be used as intermediate positions for the mass transport of C and Si through the α-SiC structure from one normal structural position to another. In many closest-packed structures such as this, there exists special one-dimensional stacking defects which produce structures called polytypes. These are alike in the two dimensions of the closest-packed planes but differ in the stacking sequence in the direction perpendicular to these planes (e.g. the ⟨0001⟩ in α-SiC). In α-SiC the most perfect polytype is called 2H and is the pure wurtzite structure in which the stacking of the hexagonal layers of Si follows the pattern ABABAB . . . . Unfortunately, by far the most common polytype in the materials of this research and in α-SiC single crystals in general is the 6H polytype with a stacking arrangement ABCACB . . . , in which the sequence reverses after every three layers. The co-ordination of both C and Si is four, regardless of polytype.

Fig. 4 shows the arrangement of Si and C atoms and the associated vacancies in one third of the 6*H* unit cell. Woodbury and Ludwig [16] have reported from electron spin resonance (ESR) spectra that C occupies three nonequivalent tetrahedral sites in 6H SiC, and Shaffer [17] has given the C co-ordinates in this polytype as 0, 0, 1/8 plus each Si position; thus, the present authors have arbitrarily depicted the C occupation of the positions located above the Si atoms.

If one takes the covalent radii of Si to be 1.17 Å [18], the size of the octahedral vacancies can be easily calculated from the 3C–SiC arrangement ($a_0 = 4.36$ Å), as the densities of both 6H and 3C are essentially identical. The result of this calculation shows the "effective" radius of the octahedral site to be 1.01 Å. As shown in Fig. 4, directly above each corner Si, e.g. atom A(1), there exists one octahedral site and two tetrahedral sites before the next Si is encountered. Using the values of the radii of Si and the octa-

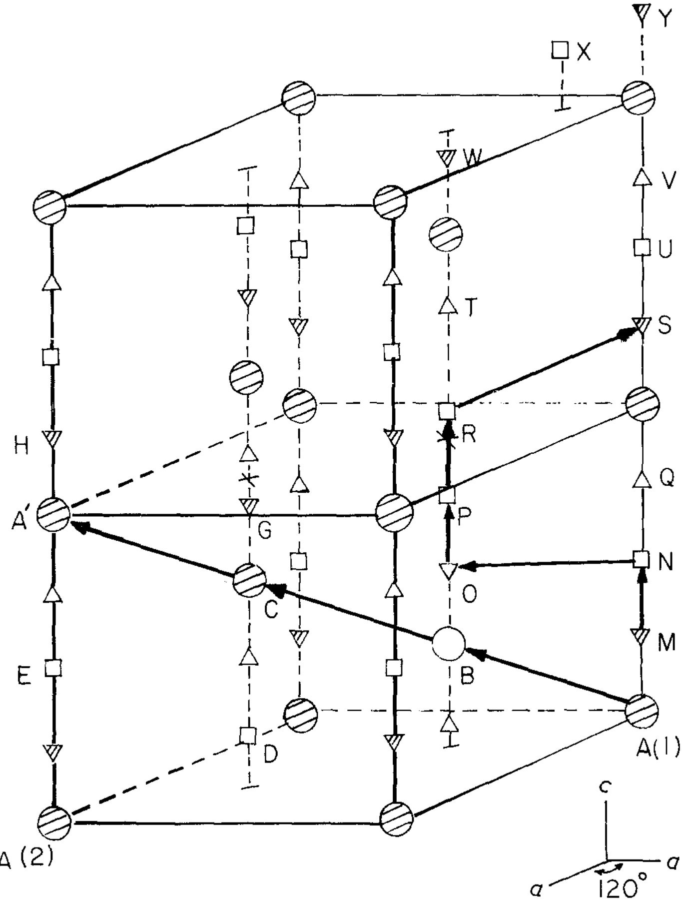

Figure 4 The arrangement of filled atomic sites, vacancies and normally unfilled tetrahedral and octahedral sites in one-third of the unit cell of 6H SiC. The ratio of c_0 to a_0 in 6H is 15.079 to 3.073 Å; however, for convenience, the figure has been shortened along the *c*-axis. The vectors indicate possible paths of C diffusion.

hedral site given above, the "effective" radius of each tetrahedral site is found to equal to 0.8 Å. From covalent radii considerations alone, C(r = 0.77 Å) would have no problem in occupying either type of vacancy whereas Si is believed to be able to occupy only the octahedral site without considerable distortion. Furthermore, a Si in a tetrahedral site would generate an untenable amount of repulsion from the slightly ionic [18, 19] surrounding Si atoms. From size considerations alone, different paths of diffusion may be chosen from Fig. 4 for both C and Si.

Since it is strongly believed that the Si does not occupy a tetrahedral site, for the reasons given above, only two transport paths are thought feasible for this species. Choosing the atoms labelled A(1) and A(2), these paths are A(1), B, C, A′ . . . and A(2), D, E, C, ... The first path is a simple vacancy jump which necessitates the presence of a nearest neighbour Si vacancy and the dilation of 2 to 4 Si atoms and one C atom. The path arbitrarily assigned to A(2) also eventually requires the presence of A Si vacancy, but considerably more total dilation is necessary to allow it to move to the two octahedral sites, D and E (especially the latter), and finally to C. It should be noted that in *each* position the Si atom has three identical choices to which to jump (assuming the atom is moving up the ⟨0001⟩ direction) because of the hexagonal symmetry. As only one

activation energy was found for the temperature range employed in this research, only one avenue of transport is thought to be operative. The path A(1), B, C, A$'$ . . . is considered to have the lower activation energy and therefore is the choice of the authors.

As for the C atom, e.g. the one labelled M, a direct jump to the required nearest neighbour C vacancy (labelled 0) is believed to be very difficult because of the considerable hinderance of the Si atoms. However, one may note from this figure that an initial jump to the vacant octahedral site (N) directly above the M site followed by a jump to the tetrahedral vacancy (O) is a much lower energy jump than the path M–O. Similar jumps from O to G and G to H can be taken by passing through the octahedral sites as P.

Since there is only one activation energy for C diffusion and C atoms at equilibrium can only reside on the tetrahedral sites above every Si atom, the most plausible path for the former is believed to be the shortest paths to the closest vacancy, i.e. M–N–O––– and similar movements such as O, P, G––– with an effective jump distance of $1/6\ C_0$.

In summary, although the exact path taken by the C and Si atoms in their movement along the ⟨0001⟩ direction cannot be precisely known, logical elimination of several avenues leaves only one choice in most cases. In any event, the self-diffusion of both species involves the zigzag movement through the SiC structure and in the case of the C atoms into normally unoccupied octahedral and tetrahedral sites.

4. Conclusions

(1) The ^{30}Si self-diffusion coefficient in the high purity α-SiC single crystals is smaller than in the N-doped crystals, in contrast to that determined for ^{14}C diffusion in the same materials. The D^*_{Si} for the former in the temperature range 2273 to 2563 K may be expressed as follows:

$$D^*_{Si} = (5.01 \pm 1.71) \times 10^2 \times \exp \frac{-7.22 \pm 0.07\,\text{eV atom}^{-1}}{kT}\ \text{cm}^2\,\text{sec}^{-1}\ \text{(pure)}$$

and

$$D^*_{Si} = (1.54 \pm 0.78) \times 10^5 \times \exp \frac{-8.18 \pm 0.10\,\text{eV atom}^{-1}}{kT}\ \text{cm}^2\,\text{sec}^{-1}\ \text{(N-doped)}.$$

(2) The difference in the values of D^*_{Si} is caused by the increase in solubility of the acceptor-type charged Si vacancies because of the presence of the donor N impurity atoms. This, in turn, increases the probability of the availability of a Si vacancy in which to accommodate the transport of this species through the crystal. This is tantamount to an "effective" decrease in the vacancy formation energy.

(3) The diffusion of Si and C through the predominantly 6H structure involves the direct movement of the former to a vacant Si site, while the transport of the latter includes the occupation of normally unoccupied octahedral and possibly tetrahedral sites.

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