

High-Temperature Oxidation of CVD β -SiC Part II. Relation between Oxygen Diffusion Coefficients and Parabolic Rate Constants

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(Received 12 May 1993, accepted 15 October 1993)

Abstract

The high temperature (1200–1550 °C) oxidation kinetics of SiC prepared by chemical vapor deposition (CVD) in dry oxygen (3×10^{-2} –80 atm) were parabolic after an initial linear step. The parabolic regime is controlled by two processes: at low temperatures and high pressures the rate limiting step is molecular oxygen permeation through the SiO₂ film; at higher temperatures and lower pressures ionic oxygen diffusion becomes the dominant process. A flux equation relating the parabolic rate constants with the molecular and ionic oxygen diffusivity confirms the existence of two parallel processes during the oxidation of CVD β -SiC. Double oxidation (¹⁶O₂/¹⁸O₂) experiments have been performed to obtain additional information about the oxygen diffusion coefficients through amorphous SiO₂ and β -cristobalite.

Die Oxidationskinetik von SiC, das durch chemischen Dampfsiederschlag (CVD) in trockener Sauerstoffatmosphäre (3×10^{-2} –80 atm) hergestellt wurde, zeigte bei hohen Temperaturen (1200–1550 °C) nach anfänglich linearem, parabolisches Verhalten. Der parabolische Bereich wird durch zwei Prozesse bestimmt: bei niedrigen Temperaturen und hohen Drücken ist der ratenbegrenzende Prozeß das Durchdringen des Sauerstoffs durch den SiO₂ Film, bei höheren Temperaturen und niedrigen Drücken ist der prozeßbestimmende Faktor die Diffusion von ionischem Sauerstoff. Eine Flußgleichung, die die Beziehung der parabolischen Ratenkonstante mit der Diffusion von ionischem Sauerstoff beschreibt, bestätigt die Existenz zweier, paralleler Prozesse während der Oxidation von CVD β -SiC. Zweifachoxidationsversuche (¹⁶O₂/¹⁸O₂) wurden durchgeführt, um zusätzliche Informationen über die Diffusions-

koeffizienten des amorphen SiO₂ und β -Cristobalits zu erhalten.

Après un départ linéaire, SiC préparé par déposition en phase gazeuse (CVD) dans de l'oxygène sec (3×10^{-2} –80 atm) s'oxyde à haute température (1200–1550 °C) selon une cinétique parabolique. Ce régime parabolique est contrôlé par deux mécanismes: à basse température et haute pression, l'étape limitante est l'infiltration de l'oxygène moléculaire dans le film de SiO₂; à plus haute température et plus faible pression, la diffusion de l'oxygène ionique devient le mécanisme dominant. L'équation des flux reliant les constantes de la croissance parabolique avec les diffusivités de l'oxygène moléculaire et ionique confirme l'existence de deux mécanismes parallèles durant l'oxydation de β -SiC produit par CVD. On a procédé à des expériences d'oxydation à deux espèces (¹⁶O₂/¹⁸O₂) afin d'obtenir des informations supplémentaires sur les coefficients de diffusion de l'oxygène dans SiO₂ et β -cristobalite.

1 Introduction

In a companion paper it has been shown that the oxidation of CVD β -SiC in dry oxygen (3×10^{-2} –80 atm) at high temperatures (1200–1550 °C) followed a linear-parabolic law similar to that used by Deal & Grove¹ to characterize the oxidation behavior of single crystal silicon.

The linear part, with activation energies close to 3 eV/at, can be related to the Si-C bond energy (3 eV/at). The parabolic regime is associated with a diffusional process. The parabolic rate constant is strongly dependent on the oxygen partial pressure, suggesting that oxygen diffusion is the rate-controlling process in this stage of oxidation. The exponent of the oxygen partial pressure dependence

changed from $n \approx 1$ at $T = 1360^\circ\text{C}$ and $P_{\text{O}_2} = 1\text{ atm}$ to $n \approx 0.7$ at $T = 1360^\circ\text{C}$ and $P_{\text{O}_2} = 1\text{ atm}$. Besides that, two sets of apparent activation energy values were found: (i) the activation energy values around 1 eV/at at low temperatures and high pressures are similar to the activation energy values reported for the oxidation of silicon,² which corresponds to permeation through vitreous silica involving activation energies around 1 eV/at with a molecular oxygen diffusion coefficient of $2.5 \times 10^{-8}\text{ cm}^2/\text{s}$ at 1200°C ,² (ii) at higher temperatures apparent activation energy values are in the range $2\text{--}3\text{ eV/at}$, showing the largest contribution of ionic oxygen diffusion to the oxidation process.

For ionic oxygen diffusion through vitreous silica the disagreement between the different authors is larger, with activation energies ranging from 1 to 4.5 eV/at depending on the authors,¹⁻⁵ although the values for the diffusion coefficients at temperatures near $1300\text{--}1400^\circ\text{C}$ agree within an order of magnitude. The diffusion coefficient determined from permeation studies is roughly 10^6 times larger than that determined by the tracer uptake and SIMS studies. As pointed out by Meek,⁶ this difference is close to the ratio in the oxygen concentration C_i (concentration of dissolved interstitial oxygen) $\approx 5.6 \times 10^{19}\text{ molecules/cm}^3$ and C_n (concentration of network oxygen) $\approx 2.2 \times 10^{22}\text{ molecules/cm}^3$, with a ratio $C_i/C_n \approx 2.5 \times 10^{-3}$.

In this case, the details of the oxidation kinetics are more complicated because of the partial crystallization of the oxide layer. Recent measurements⁷ of oxygen diffusion through β -cristobalite in bulk samples have shown lower diffusivities than in vitreous silica. This fact has been taken into account to interpret activation energy values, showing that the apparent activation energy corresponds to two processes with activation energies close to 3 and 4 eV/at , which are similar to activation energies for oxygen diffusion through amorphous SiO_2 and β -cristobalite, respectively.

The main objectives of this work were to determine the oxygen diffusion coefficients in thermally produced oxide (β -cristobalite and amorphous SiO_2) by means of ^{18}O isotope exchange experiments and to establish which oxygen diffusion process is the rate-limiting step of the oxidation during the parabolic growth by a direct comparison between the diffusion coefficients and the parabolic constant for the silica growth.

2 Experimental Procedure

2.1 Materials and ^{18}O isotope exchange experiments

The material used in this study was cubic (zincblende structure) β -SiC made by CVD. The details of this

procedure have been explained elsewhere.⁸ The resultant CVD β -SiC layers are polycrystalline (preferentially oriented over the (111) axis), highly pure and dense.

Double oxidation experiments were carried out in a controlled-atmosphere furnace that allows heating up to 1800°C . The first oxidation was performed in dry oxygen at temperatures ranging from 1240°C to 1500°C for $\approx 15\text{ h}$. The second oxidation was performed in the same furnace: after the evacuation of the oxidation chamber, oxygen-18 enriched gas is introduced without modifying the temperature. Samples were oxidized in the enriched gas for 180 or 360 min .

2.2 SIMS measurements

All samples were analyzed by secondary ion mass spectrometry (SIMS), measurements being performed on a CAMECA IMS 3f spectrometer, using a Cs^+ primary ion beam current of 200 nA , or on a Atomika A-DIDA 3000-30 ion microprobe, using an Ar^+ primary ion beam current of 500 nA . All samples were Au coated to improve the leakage of accumulated surface charges. Moreover, a focused electron gun provided charge neutralization of the sputtered surface during profiling. Four masses were simultaneously recorded: ^{12}C , ^{16}O , ^{18}O and $^{28,29}\text{Si}$. The depth of the sputtered crater was measured with a profilometer having a depth uncertainty estimated to be approximately 10% . Sputter time was converted by assuming a constant sputter rate through the silica layer. The fractional concentration of oxygen-18 was obtained by dividing the oxygen-18 signal by the sum of the two oxygen signals.

3 Results

3.1 Diffusion in thermal oxide

Five ^{18}O exchange experiments on oxidized SiC samples over the temperature range of 1240°C to 1500°C were analyzed.

As has been shown previously,⁹ at temperatures below 1450°C the thermal oxide is partially crystallized with a crystallization degree that depends mainly on the temperature and on the surface state of SiC.

Figures 1 and 2 show characteristic SIMS profiles corresponding to samples oxidized in the oxygen-18 gas enriched atmosphere at 1330°C for 160 min and at 1500°C for 180 min , respectively. The first part corresponds to the silica layer (silicon and oxygen-16 signals constant). Upon reaching the oxide/silicon carbide interface, a steep drop in the oxygen signal and an increase in the carbon signal occurs. The last region belongs to SiC, where Si and C signals are constant. The differences in the Si signal variations

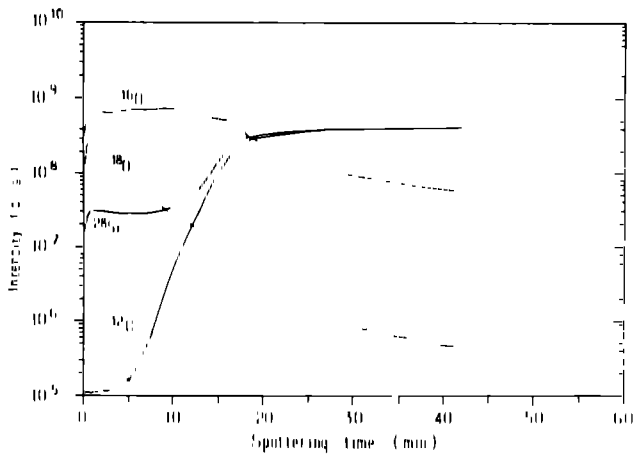


Fig. 1. Diffusion profile obtained by SIMS (Cameca Ims 31) for an oxidized SiC sample subjected to diffusion annealing in $^{18}\text{O}_2$ for $t = 160$ min at $T = 1330$ C (Ref. SiC1330)

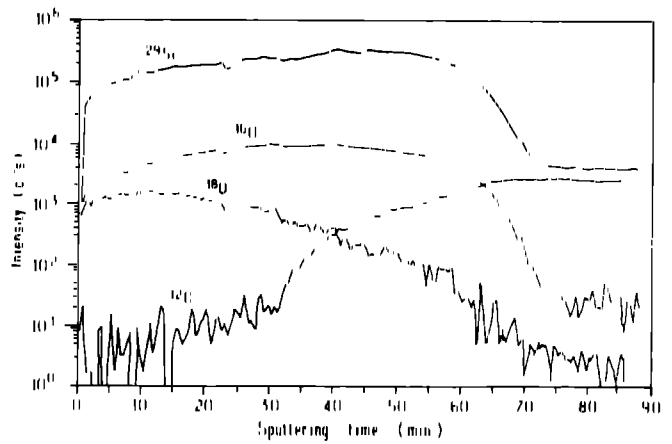


Fig. 2. Diffusion profile obtained by SIMS (Atomika A Dida) for an oxidized SiC sample subjected to diffusion annealing in $^{18}\text{O}_2$ for $t = 180$ min at $T = 1500$ C (Ref. SiC1500)

between Figs 1 and 2 come from the use of different ion sources, Cs^+ and Ar^+ , respectively. The interface width is much wider than in silicon and it increases with temperature, showing that this interface is generated by outward diffusion of the reaction products.¹⁰

The concentration-penetration curve obtained from the SIMS profile of Fig. 1, which corresponds to a partially crystallized SiO_2 layer, is shown in Fig. 3 (continuous line).

By an analogy with the results concerning bulk samples of cristobalite and partially crystallized SiO_2 ,⁵ the profiles corresponding to temperatures lower than 1450 C can be fitted using a complex solution with the sum of two complementary error functions, one with a large D (for the amorphous part) and one with a smaller one (for the crystal), together with an exponential term which is a factor allowing for some interstitial-network exchange in the oxide (β is a network interstitial coefficient), as has been defined by Kalen *et al.*¹¹

$$C(x, t) = \left(\left(\sum_{i=1}^2 A_i \operatorname{erfc} \left(\frac{x}{\sqrt{2D_i t}} \right) - 1 \right) \exp(-\beta t) \right) + 1 \quad (1)$$

where the parameter A_i gives the contribution of the different diffusion coefficients to the tracer profile and, if local diffusion between amorphous and crystalline SiO_2 can be avoided, it gives a good approximation of the crystallization percentage.

Figure 3 is an example of this kind of fitting. Equation (1) fits this profile well. The contribution of network-interstitial exchange is very low, in contrast with the results of Kalen *et al.*,¹¹ which attribute the uniform tracer concentration in their samples to this phenomenon.

For temperatures $T \geq 1450$ C the silica layer consists of polycrystalline β cristobalite and the profiles can be fitted using the Whipple solution

which takes account of a bulk diffusion coefficient and a short circuit (grain boundary) one

$$C(x, t) = C_0 \left[\operatorname{erfc} \left(\frac{\eta}{2} \right) + \frac{2\eta}{n\sqrt{\pi}} \int_1^\Delta \exp \left(-\frac{\eta^2}{4\sigma} \right) \times \left(\frac{\Delta - \sigma}{\Delta - 1} \right)^{1/2} \left[\frac{1}{\sqrt{\pi}} \exp(-X^2) - X \operatorname{erfc} X \right] \frac{d\sigma}{\sigma^{3/2}} \right] \quad (2)$$

where

$$X = \left(\frac{\Delta - 1}{\Delta - \sigma} \right)^{1/2} \frac{\sigma - 1}{2\beta} \quad \beta = \frac{(\Delta - 1)\delta}{\sqrt{D_v t}}$$

$$\Delta = \frac{D_c}{D_v} \quad \eta = \frac{x}{\sqrt{D_v t}} \quad n = L(D_v t)^{1/2}$$

where σ is the integration variable, and D_v and D_c are the bulk and grain boundary diffusion coefficients respectively. C_0 is the constant surface concentration.

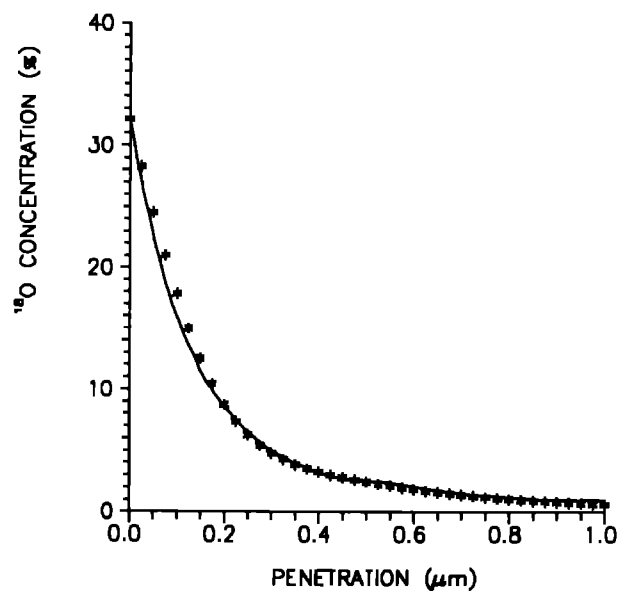


Fig. 3. Comparison between the ^{18}O experimental profile (—) of a partially crystallized oxide layer annealed at $T = 1330$ C for $t = 160$ min and that calculated (•) using two complementary error functions.

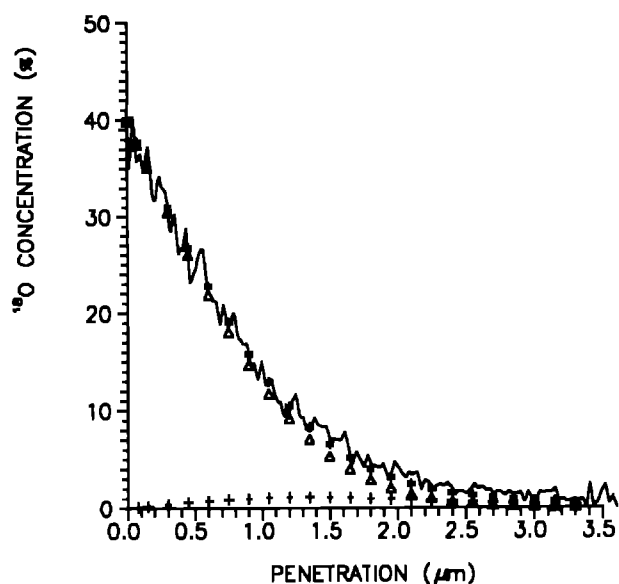


Fig. 4. Comparison between the ^{18}O experimental profile (—) of a cristobalite layer annealed at $T = 1500^\circ\text{C}$ for $t = 180$ min and one calculated using the Whipple solution Δ . Bulk diffusion (D_v), + grain boundary diffusion (D_g), +, $D_v + D_g$.

ration, δ_g the grain boundary width and $2L$ the grain size

Figure 4 shows the concentration-penetration profile for a polycrystalline cristobalite layer with the fitting obtained using eqn (2). Cristobalite invariably crystallizes with a spherulitic morphology,^{9,12} and the spherulites are disks which are quite thin compared to their diameters. Figure 5 shows a scanning micrograph corresponding to spherulites grown at 1500°C with a diameter $\approx 30\ \mu\text{m}$. This implies that the total grain boundary surface is too small with regard to the grains to have a significant effect on the profile. If the grains were

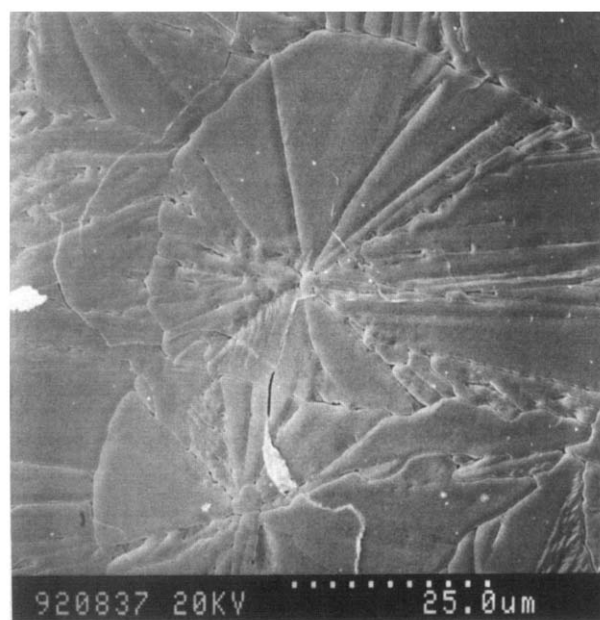


Fig. 5. Scanning micrograph of a SiC sample oxidized at $T = 1500^\circ\text{C}$ for $t = 180$ min, showing the spherulitic growth of the cristobalite

smaller we should expect an accumulation of oxygen 18 isotope at the oxide-silicon carbide interface, resulting from the high diffusivity value of oxygen through grain boundaries

Table 1 collects together the crystalline and amorphous diffusion coefficients. The similarity between diffusivities determined in this work for thermal oxide and the ones obtained in bulk silica⁷ allows an identical transport process to be considered for the two materials. Consequently, an activation energy value has been determined using data from both bulk and thermal oxides (Fig. 6), which is a composite of these data.

$$D_{am}(\text{cm}^2/\text{s}) = 1.1 \times 10^{-2} \exp\left(-\frac{3.45\text{eV/at}}{kT}\right)$$

$$D_{cr}(\text{cm}^2/\text{s}) = 5.6 \exp\left(-\frac{4.55\text{eV/at}}{kT}\right)$$

Diffusion through cristobalite is slower than through vitreous SiO_2 by a factor of 2.5 at 1500°C and 10 at 1200°C .

3.2 Comparison between parabolic constants obtained from kinetic experiments and diffusion coefficients

If it is accepted that the carbonaceous species do not play a significant role during SiC oxidation in the temperature range (1200 – 1500°C) used in this study,^{10,13} the process must then be controlled in the parabolic regime by oxygen diffusion.

As has been experimentally shown in Part I of this study⁹ and in the work of Zheng *et al.*¹³ the oxidation mechanism is a parallel transport through the oxide via molecular oxygen and ionic oxygen.

A good way to confirm this parallel transport mechanism is to establish a relation between the K_p

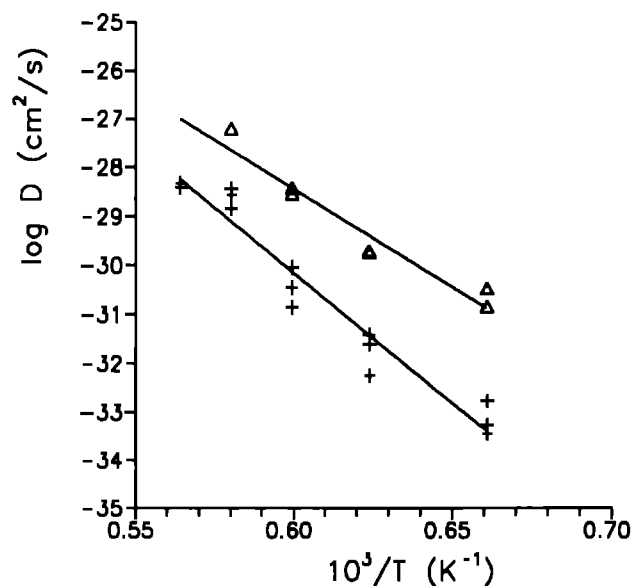


Fig. 6. Arrhenius plot of oxygen diffusivities through α SiO_2 and β cristobalite Δ , D amorphous, +, D crystallized

Table 1. SIMS diffusion coefficients for crystalline and amorphous SiO₂ in oxidized SiC

T (°C)	A_I (°a)	A_R (°a)	D_I (cm ² s)	D_R (cm ² s)	$D_I \rho_I$ (cm ³ s)	β (s ⁻¹)
1240	75	25	3×10^{-15}	4×10^{-14}	—	—
1330	80	20	1.0×10^{-14}	1.25×10^{-13}	—	2×10
1395	85	15	4.0×10^{-13}	4.5×10^{-13}	—	—
1450	100	0	3.0×10^{-13}	—	5.0×10^{-17}	—
1500	100	0	4.6×10^{-13}	—	9.0×10^{-17}	—

values, obtained from thickness versus time measurements and shown in Table 2,⁹ and the oxygen diffusion coefficients for both interstitials and network.

The oxygen flux through a thickness X_0 can be represented as¹⁴

$$\bar{J} = -\frac{C_O}{X_0} \int_{a_0^g}^{a_0^i} D_O d \ln a_O \quad (3)$$

Here C_O is the oxygen concentration in the oxide, a_O is the oxygen activity and D_O is the oxygen tracer diffusivity. The superscripts i and g refers to the inner (silicon carbide oxide) and the outer (gas/oxide) interface. The oxygen diffusivity is a function of the oxygen activity and can be expressed as

$$D_O = D_O^* P_{O_2}^n \quad (4)$$

where D_O^* is the oxygen diffusion coefficient at 1 atm pressure and the value of n depends on the defect structure.¹⁵

Thus, the flux can be written as

$$\bar{J} = -\frac{C_O D_O^*}{2nX_0} [(P_{O_2}^i)^n - (P_{O_2}^g)^n] \quad (5)$$

When the oxide growth is diffusion controlled the equilibrium partial pressure of oxygen at the SiO₂/SiC interface is very low¹⁶ ($P_{O_2}^i \ll P_{O_2}^g$), and thus the transport rate can be expressed as

$$\bar{J} = -\frac{C_O D_O^*}{2nX_0} (P_{O_2}^g)^n \quad (6)$$

For interstitial diffusion by molecular oxygen the exponential factor n is 1² and $D_O^* = 2D_{O_2}^*$,¹⁶ so

$$\bar{J}_{O_2}(\text{molec}) = -\frac{C_O D_{O_2}^*}{2X_0} P_{O_2}^g \quad (7)$$

For ionic oxygen diffusion $n \geq 0.5$,^{17,18}

$$\bar{J}_{O_2}(\text{ion}) = -\frac{C_O D_{O_2}^*}{X_0} [(P_{O_2}^g)^{1/2}] \quad (8)$$

This oxygen flux must be equal to the growing flux of silica, with a proportionality constant m which is the number of moles of oxygen required to form 1 mol of silica:

$$m\bar{J}_{SiO_2} = \bar{J}_{O_2} = \bar{J}_{O_2}(\text{molec.}) + \bar{J}_{O_2}(\text{ion}) \quad (9)$$

The growth rate of silica can be represented as

$$\frac{dX_0}{dt} = \frac{\bar{J}_{SiO_2}}{C_O} \Rightarrow \bar{J}_{SiO_2} = \frac{C_O K_P}{2X_0} \quad (10)$$

where K_P is the parabolic constant

Substituting eqns (7), (8) and (10) in (9) the relation between K_P and the diffusion coefficients can be obtained through a pressure dependence

$$\frac{m}{2} K_P = D_{O_2}^* P_{O_2}^g + D_{O_2}^* (P_{O_2}^g)^{1/2} \quad (11)$$

where the effective diffusion coefficient is calculated using the solubility and diffusivity of dissolved oxygen. These data have been taken from the work of Zheng *et al*.¹³ and the values for ionic oxygen from the experiments performed in this work and in

Table 2. K_P values obtained from thickness versus time measurements [-]

T (°C)	$(K_P) \times 10^{-13}$ (cm ⁴ s)				
	P_{O_2} (atm)				
	80	20	1	0.22	0.031
1000	$K_P = 14$	$K_P = 4.0$	—	—	—
1200	$K_P = 150$	$K_P = 7.5$	$K_P = 0.42$	—	—
1250	—	—	$K_P = 0.68$	—	—
1310	—	—	$K_P = 1.1$	$K_P = 0.40$	$K_P = 0.096$
1360	$K_P = 520$	$K_P = 28$	$K_P = 1.45$	$K_P = 0.87$	$K_P = 0.19$
1420	—	—	$K_P = 2.8$	$K_P = 1.7$	$K_P = 0.22$
1475	—	—	$K_P = 4.0$	$K_P = 3.6$	$K_P = 0.37$
1545	—	—	—	—	$K_P = 0.72$

reference.⁷ The ionic oxygen concentration at the outer interface was taken as equal to the oxygen concentration in the oxide. In the present case the problem is slightly more complicated owing to the presence of two diffusivity paths in the samples: amorphous silica and cristobalite. So, in fact, if the degree of crystallization of the oxide layer is known eqn (11) can be transformed into

$$\frac{m}{2} K_p = (\nu D_{O_2}^*(am) + (1 - \nu) D_{O_2}^*(cr)) P_{O_2} + (\nu D_{O_2}^*(am) + (1 - \nu) D_{O_2}^*(cr)) (P_{O_2})^{1/2} \quad (12)$$

where ν is the amorphous percentage and m has been taken equal to 1.5, assuming that the oxidation reaction product is $CO_{(g)}$.

Because of the lack of diffusivity data relating the molecular oxygen through β -cristobalite, it has been assumed that the diffusivity through this phase is the same as in amorphous silica. This assumption is not surprising since the six-fold rings responsible for the high diffusivity of O_2 in amorphous SiO_2 are also present in β -cristobalite. The most important difference between amorphous silica and β -cristobalite comes from the existence of five- or seven-fold rings in silica which destroy the long range order.¹⁹

With this assumption, eqn (12) can be rewritten as

$$\frac{m}{2} K_p = D_{O_2}^* P_{O_2} + (\nu D_{O_2}^*(am) + (1 - \nu) D_{O_2}^*(cr)) (P_{O_2})^{1/2} \quad (13)$$

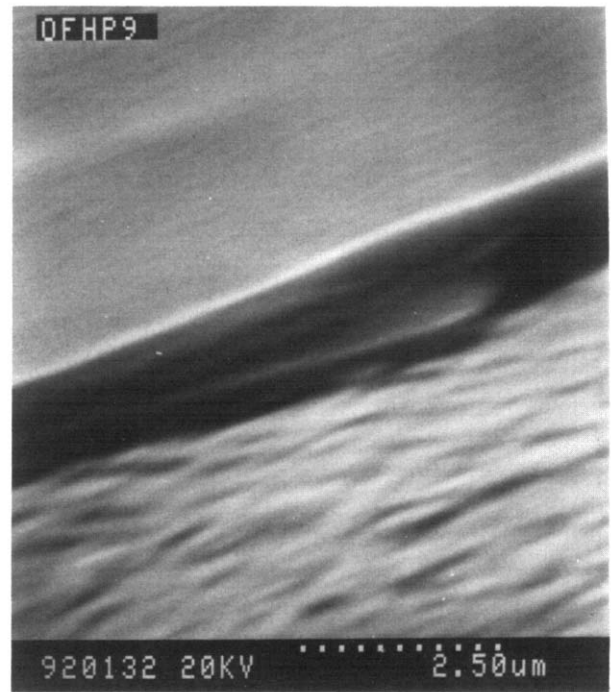


Fig. 7. Scanning micrograph of a SiC sample oxidized at $T = 1000^\circ C$, $P_{O_2} = 20$ atm and $t = 360$ min.

In Tables 3 and 4 the results for pressures of 1 and 80 atm, respectively are shown. In general, there is a good agreement between the diffusivity values obtained from SIMS measurements and kinetic values obtained via thickness determination, if the uncertainty which exists concerning the experimental data and the pressure dependence of ionic oxygen is considered.

Table 3. Comparison between the K_p and the diffusivity values for $P_{O_2} = 1$ atm. A and B represent the molecular and ionic oxygen contribution, respectively

T ($^\circ C$)	Amorphous fraction	A	B	$A + B$	$\frac{m}{2} K_p$
1200	0.80	3.1×10^{-14} (60%)	2.1×10^{-14} (40%)	4.6×10^{-14}	3.15×10^{-14}
1250	0.50	4×10^{-14} (53%)	3.6×10^{-14} (47%)	7.6×10^{-14}	5.1×10^{-14}
1310	0.35	5.45×10^{-14} (43%)	6.8×10^{-14} (57%)	1.2×10^{-13}	8.3×10^{-14}
1360	0.25	7.1×10^{-14} (33%)	1.4×10^{-13} (67%)	2.1×10^{-13}	1.1×10^{-13}
1420	0.15	9.5×10^{-14} (24%)	2.9×10^{-13} (76%)	3.8×10^{-13}	2.1×10^{-13}
1475	0.05	1.2×10^{-13} (17%)	5.7×10^{-13} (83%)	6.9×10^{-13}	3.0×10^{-13}

Table 4. Comparison between the K_p and the diffusivity values for $P_{O_2} = 80$ atm. A and B represent the molecular and ionic oxygen contribution, respectively

T ($^\circ C$)	Amorphous fraction	A	B	$A + B$	$\frac{m}{2} K_p$
1000	1	5.4×10^{-13} (99.1%)	5.0×10^{-15} (0.9%)	5.45×10^{-13}	1.05×10^{-11}
1200	0.30	2.5×10^{-12} (95.4%)	1.2×10^{-13} (4.6%)	2.6×10^{-12}	1.1×10^{-11}
1360	0	5.7×10^{-12} (88.2%)	7.7×10^{-13} (11.8%)	6.5×10^{-12}	3.9×10^{-11}

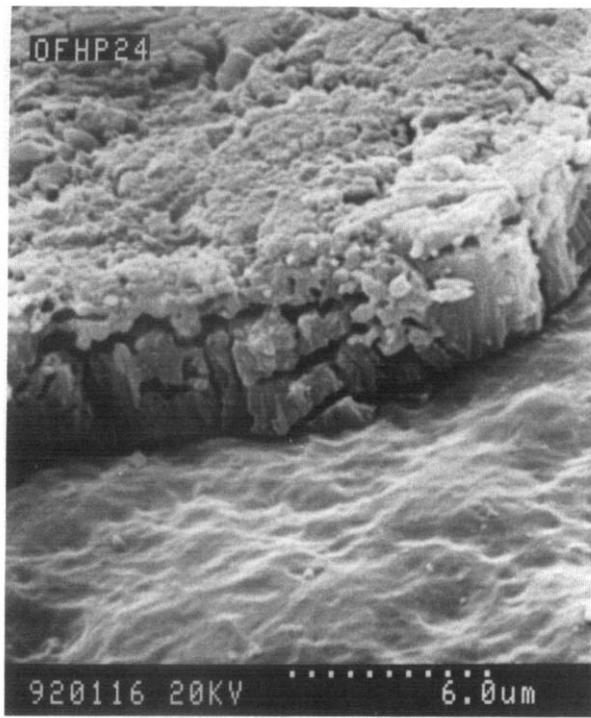


Fig. 8. Scanning micrograph of a SiC sample oxidized at $T = 1360^\circ\text{C}$, $P_{\text{O}_2} = 80\text{atm}$ and $t = 180\text{min}$

The parabolic constant corresponds to the sum of three processes: (i) interstitial diffusion of molecular oxygen, (ii) ionic oxygen diffusion through amorphous silica and (iii) ionic diffusion through cristobalite.

Another fact is that, as expected a priori, the interstitial contribution increases as temperature decreases and pressure increases and vice versa ionic contribution becomes dominant at high temperatures and low pressures.

The molecular oxygen contribution is especially clear in the experiments at 1000°C and 80atm (Table 4) where the oxide layer is completely amorphous and there is no presence of short circuits (Fig. 7). If in this case only ionic diffusion had been considered there would have been a discrepancy with the K_p value of the order of 500.

At higher temperatures and $P = 80\text{atm}$ there is a large difference (K_p - diffusivity values) which can be easily explained in terms of the high porosity of the oxide (Fig. 8). To account for this fact a factor to represent short circuit diffusion should be included in eqn (13).

4 Conclusions

The oxidation kinetics of CVD β SiC has been described using a flux balance equation which compares oxygen diffusion coefficients and parabolic rate constants through a pressure dependence.

This equation takes account of parallel transport of oxidants via molecular oxygen and ionic oxygen

and the presence of two different SiO_2 phases (amorphous and β cristobalite) in the oxide layer. The molecular oxygen diffusion coefficients have been taken from the article of Zheng *et al.*¹³

Double-oxidation experiments of CVD β SiC were carried out first in $^{16}\text{O}_2$ and then in $^{18}\text{O}_2$ -enriched environments. Oxygen isotope profiles were measured by secondary ion mass spectrometry. The concentration-penetration profiles obtained from SIMS data were used to determine the lattice oxygen diffusion coefficients through amorphous SiO_2 and β cristobalite.

The comparison between these diffusivity data and the K_p values through the flux equation (eqn (13)) confirmed the existence of parallel transport via molecular and ionic oxygen.

The influence of molecular oxygen permeation is clear from the results at $P_{\text{O}_2} = 80\text{atm}$ and $T = 1000^\circ\text{C}$. When temperature increases and pressure decreases the ionic oxygen contribution rises to $\approx 97\%$ at $T = 1540^\circ\text{C}$ and $P_{\text{O}_2} = 0.03\text{atm}$.

Acknowledgements

The authors are indebted to Prof. R. W. Cahn for correction of the manuscript and for valuable discussions. J.R.V. and M.T.C.M. wish to acknowledge financial support from CICYT (project MAT 92.0501).

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