

Pressure dependence of SiO₂ growth kinetics and electrical properties on SiC

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(Received 10 August 2007; accepted 13 November 2007; published online 31 January 2008)

Dry oxidations between 0.25 and 4 atm at 1150 °C are used to characterize the pressure dependence of the growth kinetics of SiO₂ along three orientations of the 4H-SiC polytype. The growth curves are studied using the Deal-Grove model. The extracted linear and parabolic constants are found to scale linearly with the pressure up to 2 atm. However, the data indicate that the (0001) Si-face exhibits a retarded growth rate above 2 atm. It is also found that, like Si, there is a critical oxide thickness below which the linear-parabolic model cannot be applied. This value is found to be between 36 and 40 nm for SiO₂ on 4H-SiC, and is apparently independent of the crystal orientation and oxidation pressure. The extracted critical thickness and its properties are similar to what is observed on Si, suggesting that the fast growth regime is dictated by the nature of the oxide. Finally, it is shown that the density of interface states (D_{it}) on the (0001) Si-face is not reduced by faster oxide growth rates within the monitored energy window. © 2008 American Institute of Physics. [DOI: 10.1063/1.2832408]

I. INTRODUCTION

The formation of passivating layers is a topic of particular interest in all electronic materials systems. In semiconductors, the creation of a high-quality passivating and insulating layer is the critical step for high-performance metal-oxide semiconductor field-effect transistors (MOSFETs) and other surface-sensitive devices.¹ The classic example is the formation of the SiO₂ layer on silicon, which underlies all of silicon MOS technology. The growth of the oxide layer has its roots in the so-called “linear-parabolic” description of Deal and Grove.² Although still not completely understood, particularly with respect to the growth of the initial monolayers of the oxide,^{3–5} the Deal-Grove (DG) model nicely describes oxide growth kinetics in terms of experimental and theoretical parameters, such as temperature and oxygen pressure. This model of growth, and its agreement with experiment, forms an underpinning for all silicon oxidation that has stood the test of time.

Silicon carbide is a wide band-gap semiconductor that also forms a silicon dioxide passivating layer upon oxidation. Considerable effort in recent years has shown that this insulating layer is essentially pure SiO₂, and forms a sufficiently good surface termination to allow SiC MOSFETs.⁶ Such SiC-based devices promise operation at extreme voltages and temperatures useful in a wide variety of applications not accessible to silicon.^{7,8} The oxidation process for SiC is significantly more complicated as the growth rates are a strong function of the crystal face and the fundamental process requires elimination of the carbon species.^{9–12} Nevertheless it

has been shown that the growth kinetics are Deal-Grove like (linear-parabolic) and can be described within their original framework.^{9,13–18} SiC oxidation is a vital step in the ultimate realization of a SiC technology and requires the same scrutiny as has been given to silicon, namely a test of oxidation models with significant parameter variation.

In this paper we present results on the pressure dependence of dry 4H-SiC oxidation above and below the standard 1 atmosphere. We observe that the predicted pressure dependence of the DG model is well verified in almost all cases, with the oxygen pressure varying from 0.25 to 4 atmospheres. Detailed experimental results are presented and analyzed in terms of SiC oxidation models. We note that some interesting deviations from the predicted pressure dependence are observed on the (0001) Si-face, the most commonly used surface for devices.

These results have additional significance in light of the current interest in the SiO₂/4H-SiC system. Recent reports show that oxidation in the presence of alumina including various metallic impurities results in a higher oxidation rate and an improved electrical interface over that grown in a conventional system (no alumina). The mechanism for this improvement is not yet understood, but it has been hypothesized that the enhanced rate might be directly responsible.^{19,20} One can imagine different tradeoffs between the expulsion of carbon and growth of the oxide that may favor the high rate process, or other catalytic mechanisms. Our results allow a direct examination of the growth rate dependence of the electrical properties at a given temperature (1150 °C). We find that the interface state density, a critical factor in device performance, is not improved by faster growth rates between 0.2 and 0.6 eV from the 4H-SiC conduction band edge.

These results provide a significant verification of the ap-

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TABLE I. Equilibrium concentration of O₂ in the oxide (10¹⁶ cm⁻³) at 1150 °C.

Pressure (atm)	0.25	0.5	1	2	4
C^*	1.13	2.26	4.52	9.04	18.08

plicability of DG-type parametrization of the oxidation of SiC, with a few outstanding anomalies. They supply the basis for scaling to new regimes of temperature and pressure in applications, as well as new data to be tested by SiC oxidation models.

II. GROWTH KINETICS

In this section we review the linear-parabolic model for Si oxidation and then apply it to the SiC system, accounting for a more complicated substrate. From these equations, the expected pressure dependence and rate are extracted.

The linear-parabolic model for silicon oxidation, proposed by Deal and Grove,² relies on the assumption that the flux of oxidant molecules is constant across the gas, oxide, and interface. It predicts the combination of two growth regimes, each governed by a different rate-limiting mechanism. The anticipated relationship between SiO₂ thickness and oxidation parameters is as follows:

$$x^2 + Ax = B(t + \tau), \quad (1)$$

where τ defines the time it takes to grow the layer of oxide present on the surface before oxidation. Constants B and A are defined below, in the case of a first-order oxidation reaction,

$$B \equiv \frac{2D_{\text{eff}}C^*}{N} \quad (2)$$

and

$$A \equiv 2D_{\text{eff}}\left(\frac{1}{k} + \frac{1}{h}\right). \quad (3)$$

Here, D_{eff} is the effective diffusion coefficient of the oxidant species through the oxide, C^* is the equilibrium concentration of the oxidant in the oxide, N is the number of oxidant molecules incorporated into a unit volume of the oxide layer, k is the reaction rate coefficient of the oxygen at the semiconductor surface, and h is the gas transport coefficient for the oxidant molecules in the gas phase. Equation (1) can be put in the form

$$x = \frac{-B}{2B/A} + \frac{B}{2} \sqrt{\frac{1}{(B/A)^2} + \frac{4(t + \tau)}{B}}. \quad (4)$$

At the extremes of rate-limiting processes, Eq. (4) reduces to simplified expressions. When the oxide is thin, growth is limited by the reaction rate, and thickness is a linear function of time, the proportionality factor being B/A , the linear rate constant. At large thicknesses, the rate is governed by the diffusion of oxidant species through the oxide, and growth enters a parabolic regime characterized by B , the parabolic rate constant.

Although in the DG model τ is used to describe a layer of oxide present on the semiconductor before oxidation, it

can also be related to a regime of fast growth rate that does not behave according to linear-parabolic kinetics.³⁻⁵ At small times and thicknesses less than ~ 35 nm, the oxide growth rate is exponential and gradually becomes linear as in the DG model. This critical thickness highlights a regime where linear-parabolic kinetics are not valid.

The DG model can also be applied, with modifications, to the more complicated SiC oxidation. The derivation accounts for the outdiffusion of the CO gas that is a byproduct not present in Si oxidation.⁹ The new linear rate constant is

$$\frac{B}{A} \approx \frac{C^*}{N} K_f, \quad (5)$$

where K_f is the forward reaction rate constant. We use an additional factor of 2, in accordance with recent corrections to our previously published model (Ref. 9).

In SiC oxidation, the rate-limiting step of the parabolic regime is unclear. If the O₂ indiffusion is limiting, then the parabolic rate constant becomes¹

$$B \approx \frac{2C^*}{1.5N} D_{O_2}. \quad (6)$$

If the outdiffusion of the CO byproduct gas slows the process, then the parabolic rate constant is expressed as

$$B \approx \frac{2C^* K_r}{N K_r} D_{CO}, \quad (7)$$

where K_r is the reverse reaction rate constant, and D_{CO} is the diffusion coefficient of the CO gas through the oxide. Here, B and B/A are effective parabolic and linear rate constants; they are derived by assuming a single-step first-order oxidation reaction. In practice, they could describe a multistep process of competing elements. Their value accounts for the overall rate-limiting speed and not the individual steps in the oxidation process. SiC experiments show that the time needed to grow an oxide thickness similar to one grown on Si is increased and that the linear rate constant is smaller on all faces, indicating a slower oxidation reaction process.

The pressure dependence of the growth rate in the DG model arises from the expressions for the linear and parabolic rate constants, which are both linearly proportional to the equilibrium concentration of oxidant species. By Henry's law

$$C^* = k_H p, \quad (8)$$

where p is the partial pressure of the oxidant species and k_H is Henry's law constant. Therefore, B and B/A are predicted to be linearly proportional to the pressure. The expected equilibrium values for C^* at various pressures are reported in Table I. Henry's law constant is calculated from reported values of C^* for SiO₂ grown at 1000 °C and 1 atm on Si.¹ At 1150 °C, k_H is 4.52×10^{16} cm⁻³ atm⁻¹.

Accounting for the pressure dependence in Eq. (4), a relationship between oxide thickness, time, and pressure can be established,

$$x = -\frac{\beta}{2\alpha} + \sqrt{\frac{\beta^2}{4\alpha^2} + \beta p(t + \tau)}, \quad (9)$$

where β and α are proportionality constants of B and B/A to pressure. This shows that the oxide thickness is a function of the product of time and pressure in the case of a single first-order oxidation reaction. For a given thickness, only the product of p and $t + \tau$ must remain constant, enabling control of the oxidation rate with pressure. Increasing the oxygen partial pressure reduces the time (i.e., the thermal budget) needed to reach a given thickness, leading to faster and cheaper fabrication of devices.

III. EXPERIMENTAL

The 4H-SiC samples were 5×5 mm, cut from single-side polished (0001)/(000 $\bar{1}$)-oriented (research grade, n -type, 8° off axis), and (11 $\bar{2}$ 0)-oriented (research grade, n -type, on axis) wafers supplied by CREE Inc.

Samples were cleaned by TCE, acetone, methanol, and HF in successive steps. Some of the (0001) Si-face substrates, selected for electrical measurements, were further cleaned using the standard RCA steps.

All samples were oxidized in a 55 mm outer diameter thick-walled glass tube inside a Thermcraft 3-zone furnace at 1150 °C. They were loaded at 900 °C and ramped up to 1150 °C at 1 atm in flowing Ar (thickness measurements) or in flowing O₂ (electrical measurements). Dry oxidations were performed at 0.25, 0.5, 1, 2, and 4 atm.

For runs below 1 atm, a flow of 0.05 L/min was maintained with an adjustable bellow valve coupled to a vacuum pump. Oxidations at 1 atm were performed in O₂ flowing at 0.25 L/min. High-pressure oxidations utilized an adjustable release valve and an oxygen flow of 0.05 L/min. Following oxidation, the tube was brought back to 1 atm and Ar was flown. The samples used for electrical characterization were then annealed for 30 min at 1150 °C prior to ramp down in order to reproduce our usual processing scheme for SiC capacitors.²¹

Oxide thicknesses were measured using an M-2000DI J. A. Woollam Co. Inc. spectroscopic ellipsometer. For oxides thinner than 15 nm, Rutherford backscattering and ion channeling were used to confirm the ellipsometry measurements, which were found to be in good agreement. Once the thicknesses were obtained, the same samples were put back into the tube for further oxidation.

Al metal gate contacts (500 μ m in diameter) were evaporated on the Si-face samples oxidized at 0.25, 1, and 4 atm used for electrical measurements in order to obtain MOS capacitors. Simultaneous high and low-frequency capacitance-voltage (C - V) measurements were then performed using a Keithley model 82 to determine the interface state density (D_{it}).

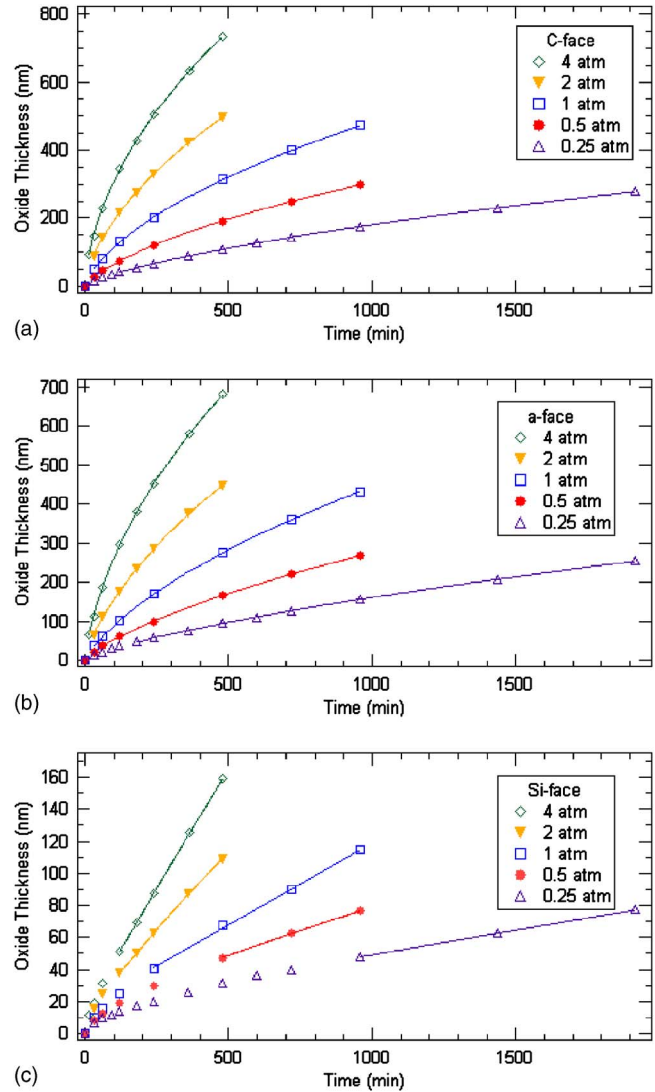


FIG. 1. (Color online) Oxide thickness as a function of time for dry thermal oxidation of 4H-SiC at pressures of 0.25, 0.5, 1, 2, and 4 atm at 1150 °C on the (a) (000 $\bar{1}$) C-terminated face; (b) (11 $\bar{2}$ 0) a -face; and (c) (0001) Si-terminated face. Solid lines are DG fits to thicknesses above X_c .

IV. RESULTS AND DISCUSSION

In this section, we first describe how we determine a critical thickness for the oxidation of 4H-SiC. This results in a τ parameter that must be used to accurately describe oxide growth on SiC using a linear-parabolic model. We then show the extracted values of the linear and parabolic rate constants at different pressures and highlight an anomaly on the Si-face at 4 atm. Finally, we demonstrate the effects of growth rate on the D_{it} at the SiO₂/SiC interface. Growth data for all pressures and substrate orientations are shown in Fig. 1.

A. Initial oxidation

As previously noted, the parameter τ is related to a critical thickness below which the DG model does not apply. While it is not normally used in the modeling of SiC oxidation, our studies show that growth curves at small thicknesses deviate from a linear-parabolic regime similarly to

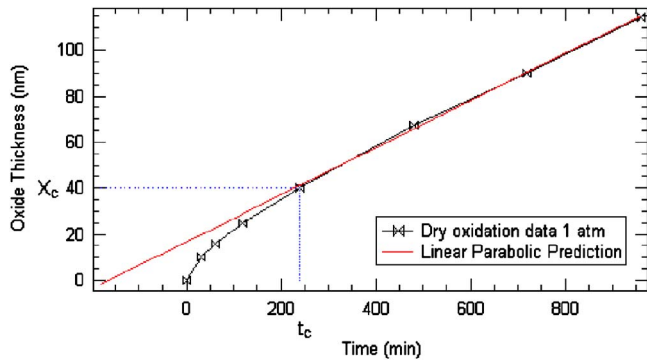


FIG. 2. (Color online) The fit of the linear-parabolic relationship to oxidation data in dry oxygen at 1 atm on the (0001) Si-face at 1150 °C. Point (X_c, t_c) denotes the onset of the linear-parabolic kinetics. The deviation from the Deal-Grove model at small times and thicknesses is evident.

SiO₂ on Si as illustrated in Fig. 2. Therefore, all fits to the linear-parabolic model must exclude points below the determined critical thickness X_c .

Several methods exist for determining the critical thickness.³ The most appropriate to our results is fitting the oxidation data to the DG equation from point (X, t) to the largest point taken (X_f, t_f) . If (X, t) is less than the critical thickness, then the growth deviates from linear-parabolic kinetics and the fit will have a large error. When X corresponds to X_c , the error in the fit is minimized as no nonlinear contribution from the accelerated growth is considered. The point where the constant fit error begins is taken to be the critical thickness.

Table II shows the results of applying the above technique to our 0.25 atm data. The uncertainty in these values comes from the limited number of measured thicknesses. Reported ranges are the closest data points on either side of X_c . Error propagation prevents thickness measurements for samples oxidized less than 15 min apart. Data from 0.25 atm represent the most precision, as there are a greater number of points below the critical thickness and they yield the values reported. We have no evidence that X_c changes with pressure. Therefore, all growth curves are fit to the DG equation excluding thicknesses less than X_c (≈ 36 nm) and incorporating τ .

Not only is the extracted value of X_c similar to the one reported for Si (35 nm),³ but it also appears to be independent of crystal orientation and oxidation pressure. This agrees well with the recent results of Yamamoto *et al.*, who reported that the extent of the accelerated growth on SiC does not vary with oxidation temperature either.²² These properties of the critical thickness are analogous to those observed in the case of silicon oxidation.^{4,5} Since the reaction mechanisms are so different between Si and SiC, this suggests that the fast-growth regime is dictated by the nature

TABLE II. Critical thickness X_c (nm).

Face	Oxide thickness
C-face	34–42
<i>a</i> -face	36–46
Si-face	36–40

TABLE III. τ (min) at 1150 °C.

Pressure (atm)	0.25	0.5	1	2
C-face	46.75	12.93	11.12	7.88
<i>a</i> -face	50.22	20.47	11.23	8.94
Si-face	347.19	186.46	95.09	31.83

TABLE IV. Parabolic rate constant B (nm²/min).

Pressure (atm)	0.25	0.5	1	2
C-face	75.65	151.79	327.4	713.99
<i>a</i> -face	75.22	157.46	343.99	755.69

TABLE V. Linear rate constant B/A (nm/min).

Pressure (atm)	0.25	0.5	1	2
C-face	0.29	0.77	1.64	3.54
<i>a</i> -face	0.23	0.51	1.02	2.03
Si-face	0.04	0.08	0.13	0.26

of the oxide. This important conclusion should help elucidate the physics behind accelerated growth and should be tested against existing models.^{5,23–26} For example, it has been proposed that when the bare surface of Si is exposed to O₂, oxygen molecules can diffuse in the semiconductor, accelerating the growth.⁵ However, the solubility of the molecular oxygen in SiC is two orders of magnitude smaller,^{27,28} which likely invalidates that particular model. A more extensive discussion is of course required to consider all existing models. This is outside the scope of this paper and will be the subject of a separate publication.

B. Extraction of growth parameters

As mentioned above, the pressure dependence of the oxidation kinetics is reflected in the linear and parabolic rate constants. These are extracted using Eq. (4) and 36 nm as a critical thickness. The results are reported in Tables III–V. Note that the values of τ are not negligible, stressing the fact that this parameter should be used when modeling SiC oxidation by a linear-parabolic equation. Figure 3 shows the linear and parabolic constants plotted as a function of pressure and their fit to a linear relationship. As described in Sec. II, the constants' linear scaling with pressure is predicted by the DG model and Henry's law. The fact that the values for B of both the C- and *a*-faces are almost equal at any given pressure suggests that, from Eqs. (6) and (7), the CO outdiffusion is not the rate-limiting step in SiC oxidation in those cases. Indeed, the O₂-indiffusion-limited parabolic rate constant is not orientation dependent, while the CO-outdiffusion-limited parabolic rate constant scales with the ratio of reaction rate constants which are unique to each face. Moreover, in the case of 1 atm dry oxidation at 1150 °C, the parabolic rate constant for Si divided by 1.5 [normalizing factor, see Eqs. (2) and (6)] is approximately 330 nm²/min, similar to the values obtained on the C-face and on the *a*-face as shown in Table IV. Accurate values for the parabolic rate

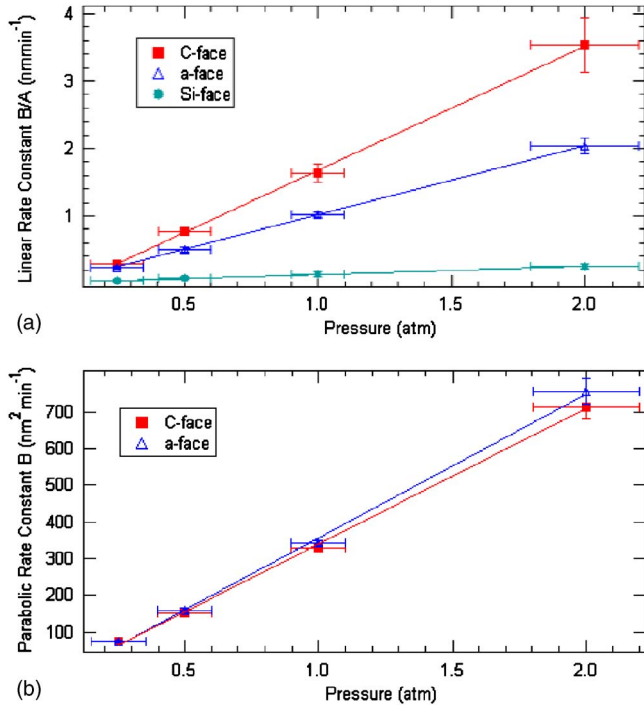


FIG. 3. (Color online) (a) Linear rate constant as a function of pressure for the (000 $\bar{1}$) C-, (11 $\bar{2}$ 0) *a*-, and (0001) Si-faces of 4H-SiC. (b) Parabolic rate constant as a function of pressure for the (000 $\bar{1}$) C- and (11 $\bar{2}$ 0) *a*-faces of 4H-SiC. The pressure dependence of the constants is modeled well by a linear law between 0.25 and 2 atm.

constant on the Si-face could not be obtained because the thickness of the oxide on this face was not sufficient to reach the onset of the parabolic growth regime.

The linear rate constant B/A also scales linearly with the pressure for all three studied SiC faces between 0.25 and 2 atm. In this regime, the differences in B/A between faces are more pronounced because the kinetics is governed by the reaction rate constant, which depends on crystal orientation. Actually, the linear reaction rate seems to scale with the density of the carbon atoms on the surface. Indeed, the ratio of B/A for the C-face to the *a*-face is about 1.6, which is close to the ratio of the amount of carbon on the two faces (1.21 to 0.74×10^{15} atoms cm^{-2}). Ideally, the Si-face has no carbon on the surface and the rate is considerably smaller.⁹ These observations suggest that the carbon, which distinguishes the SiO_2/SiC system from the SiO_2/Si system, plays a key role in the oxidation process and might be the reaction rate determining factor.

So far, we have omitted the 4 atm data because the lack of thicknesses measured below the onset of the parabolic regime prevents us from extracting accurate rate constants for the *a*-face and the C-face. However, we were able to analyze the Si-face up to that pressure.

While we have shown that the pressure dependence of the reaction rate between 0.25 and 2 atm can be modeled by a linear law, it seems to no longer be the case at 4 atm on the Si-face, as evidenced in Fig. 4. Indeed, the linear rate dependence is then more accurately described by $p^{0.4}$. To better illustrate this change in behavior, we plot thickness versus pressure*time curves for 0.25, 1, and 4 atm in Fig. 5. Ac-

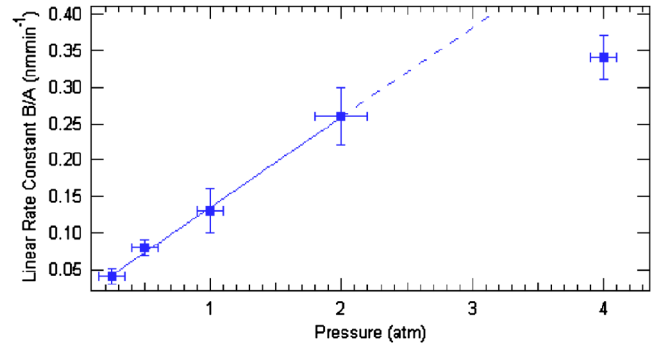


FIG. 4. (Color online) Linear rate constant as a function of pressure for the (0001) Si-terminated face. The line is the linear fit to B/A from 0.25 to 2 atm. The 4 atm point does not fall on the curve, which reveals a sublinear pressure dependence in that range.

ording to Eq. (9), these curves will be shifted along the normalized time axis in the presence of a nonzero τ . However, at a given thickness, the slopes (proportional to the growth rate) are expected to be equal. This is of course if the dependence of the rate constants on the pressure is linear. Such normalized curves are thus a direct way to study the validity of the derived DG model and of Henry's law using the raw data, since no fit is needed. We note that the normalized slopes for the C- and *a*-faces (not shown, all curves are on top of each other because of smaller τ values) agree well over all pressures, and it can be assumed that their growth rates depend linearly on pressure up to 4 atm. For the Si-face, however, the normalized slope is almost equal at 0.25 and 1 atm but is smaller at 4 atm. This supports the sublinear pressure dependence of the rate constant at 4 atm shown in Fig. 4 which was extracted from the DG fit.

Sublinear pressure dependence of the growth rate has been observed in some cases for Si oxidation,^{29–31} and attempts have been made to relate it to specific reaction mechanisms.^{32,33} In particular, such a dependence is expected if several oxidation reactions (of different orders) involving the decomposition of O_2 molecules into atomic oxygen take place simultaneously. Under specific assumptions, Ghez and van der Meulen have shown³² that if the insertion of atomic oxygen is the primary oxidation process, the growth rate becomes proportional to $p^{0.5}$. As oxidation reactions involving both atomic and molecular species are

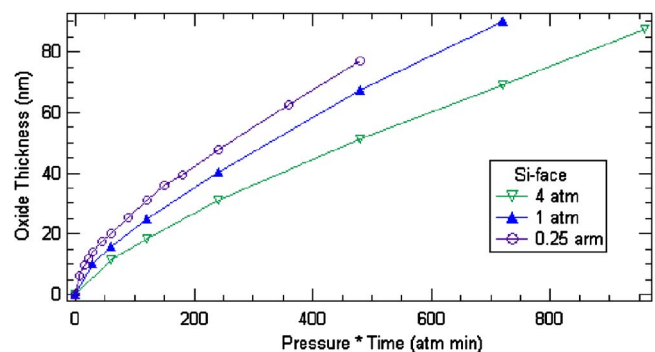


FIG. 5. (Color online) Oxide thickness on the (0001) Si-face as a function of the product of pressure and time for 0.25, 1, and 4 atm. The reduced slope of the 4 atm data at any given thickness indicates a retarded growth rate at this pressure (i.e., a sublinear pressure dependence).

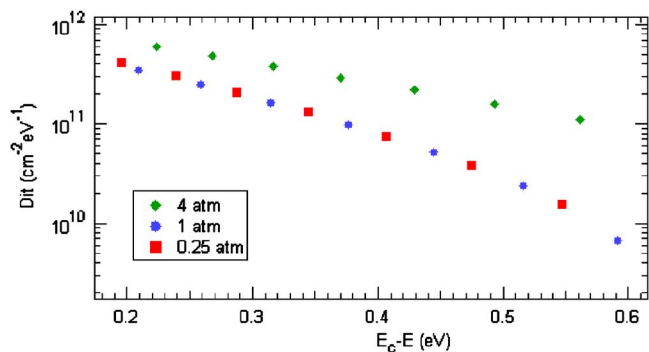


FIG. 6. (Color online) Measured interface trap densities in the upper part of the band gap for oxides grown at 0.25, 1, and 4 atm on the (0001) Si-terminated face.

thought to occur in parallel, the dependence is predicted to be of the form p^γ , where the value of γ is between 1 and 0.5, depending on the dominating reaction. The same conclusions can be applied to SiC oxidation; if the sublinear pressure dependence is observed on the Si-face only, it could mean that the O_2 reaction rate is so slow in that case that it allows for secondary reactions (e.g., the inclusion of atomic oxygen) to weigh more in the overall process.

Another possible explanation for the sublinear pressure dependence is that the slow reaction rate on the Si-face leads to a reaction-limited regime which extends over larger SiO_2 thicknesses. Consequently, the O_2 concentration gradient across the oxide is small (C_{O_2} at the interface is close to C^*) even for thicker oxides, which requires the indiffusion of more oxygen molecules to achieve equilibrium. Increasing the pressure exacerbates this phenomenon and it could be that, although Henry's law is still valid (as suggested by the a -face and the C -face data), the time required to achieve equilibrium becomes too long and the oxidation is not a steady-state process.

C. Electrical properties of the interface

Measuring the D_{it} of SiC/ SiO_2 interfaces with similar oxide thicknesses (≈ 40 nm), grown at different pressures allows us to test the theory that an increased growth rate will enhance the interface quality. After performing $C-V$ measurements on our samples, we conclude from Fig. 6 that an increased growth rate does not decrease the D_{it} , and that oxidizing at 4 atm actually increases the number of traps within the upper part of the band gap. The exaggerated increase in D_{it} at 4 atm coincides with the Si-face anomaly. This could be the result of a different rate-limiting process in the high-pressure oxidation regime of the Si-face, a process that could lead to a wider transition layer and/or to C buildup at the interface, subsequently increasing the D_{it} . In any case, it can be inferred that increased growth rates observed in alumina enhanced oxidation processes do not directly contribute to the D_{it} reduction and that some other mechanisms, such as interactions with a metal impurity (e.g., sodium), must be responsible for improving the inversion layer mobility.^{19,20}

V. CONCLUSIONS

We have shown that between 0.25 and 4 atm, the kinetics of thermal oxidation of 4H-SiC can be studied using the Deal-Grove linear-parabolic model. As for silicon, it is not applicable to SiC below a critical thickness (36 to 40 nm) and it is therefore necessary to employ τ to properly characterize oxide growth.

Agreements of the critical thickness on all faces and with Si, as well as its lack of sensitivity to processing parameters, hint that the departure from the linear-parabolic model at small thicknesses may be a property of SiO_2 only.

The linear and parabolic rate constants scale linearly with pressure up to 2 atm for all faces. However, at 4 atm the Si-face growth rate is better predicted by a sublinear law, revealing the presence of a different rate-limiting process. This process is suspected to increase the density of interface defects.

Using variable pressure, we also determined that enhancing the growth rate at a given temperature does not decrease the density of interface states within the monitored energy window, and that the accelerated growth in the presence of alumina is probably not by itself responsible for better device properties.

We finish by noting that increasing the oxidation pressure not only allows for accelerated growth rates at a given temperature but also makes possible the oxidation of SiC at lower temperatures in shorter times. The temperature dependence of the oxide and of the interface properties at a given rate are indeed currently under investigation. We will shortly know if SiC devices could be fabricated in Si-like conditions.

ACKNOWLEDGMENTS

We thank Tommy Howe, John Fellenstein, and Robert Patchin for their assistance in the creation of our oxidation tube and high-pressure setup. This work was supported by DARPA/ONR under Contract N00014-12-1-0628.

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