Oxidation kinetics of single crystal silicon carbide using electron microscopy

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The thickness of the specific oxide phase scale formed on single crystal silicon carbide was measured to determine the activation energy on both the Si-face and the C-face. The oxide scales were thermally formed on both the Si- and the C-face of 6H-SiC at 1273–1473 K in a pure oxygen environment. Microstructures of the oxide scales were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Crystalline oxide scales were found to be randomly distributed on the surfaces of both the Si-face and the C-face of the oxidized samples. The focused ion beam (FIB) micro-sampling technique was employed to prepare the specific site specimens for thickness measurement of the oxide scales in the regions where the oxide scales were composed of only uniform amorphous silica. The thickness of the oxide scales was measured directly to high accuracy using SEM and TEM, and fitted to the Deal–Grove model. The oxidation activation energy for the parabolic rate constant was found to be 358 kJ/mol for the Si-face and 85 kJ/mol for the C-face. The low activation energy for the C-face that is close to that for oxygen diffusion in silica strongly suggested that the rate controlling process of the C-face oxidation is the diffusion of oxygen in the oxide layer.

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1. Introduction

Silicon carbide (SiC) has many excellent properties that make it suitable for use as a structural material as well as a functional material in various applications. Those properties include high chemical stability, high sublimation temperature and high thermal conductivity. It also possesses excellent electrical properties such as, wide band gap, which is approximately three times larger than that of silicon, high electric field break down strength, which is about one order higher than that of silicon, and high saturated drift velocity. Beside these superior electrical properties, the operating temperature of SiC (up to about 650 K) is much higher than that of silicon devices (generally about 400–450 K). These properties make SiC a promising candidate as a replacement for silicon in high power, high frequency, and high efficiency semiconductor devices.

At high temperatures, in a sufficient oxygen partial pressure environment, protective silica oxide scales are known to form on SiC. These oxide scales can serve as a protective film in various processes. Over the years many studies have been conducted on the oxidation of SiC.1)–7) However, many aspects in the oxidation of SiC still remain unclear, such as the oxidation mechanisms, the microstructures of the oxide scale, and the interface between the oxide scale and the SiC. One of the main reasons for the lack of clarity of the oxidation mechanisms is the wide variation of the data in the reported oxidation rates and the oxidation activation energies. Presumably, the origins for differences in reported oxidation rates, which then lead to different estimated activation energies, were the differences in the samples used, the experimental conditions, the experimental procedures, or the methods for the evaluation of the oxidation rate.

Previously, we characterized the microstructures of the oxide scales formed on a SiC sample oxidized in pure oxygen at 1473 K for 16 h.8) Figure 1(a) shows an optical microscope (OM) image of the Si-face of the sample after oxidation. Glossy patterns were observed to be distributed randomly on the surface of the sample. Figures 1(b) and 1(c) show the cross-sectional TEM images of the specimens taken from region A, the region without patterns, and region B, the region with the glossy pattern, respectively.
amorphous oxide layer, as indicated by the inset of the selected area diffraction pattern, from region A has a uniform thickness. However, the thickness of the oxide scales from region B is not even and consisted of both crystalline and amorphous silica. The oxide scale thickness of this region varied from 15 to 30 percent thicker than the oxide scale from region A. As shown by Chayasombat et al., the thickness of oxide scales where crystalline phase silica existed could vary from a few percent to more than 100 percent thicker than the region where the oxide scale was composed of only amorphous silica.

In previous studies on oxidation kinetics of SiC by other investigators, the most frequently used methods for the oxide scale thickness measurement were gravimetry or ellipsometry. These methods measured the thickness of the formed oxide scales from unspecified and relatively wide regions of the samples, which to some extent possibly lead to the errors in thickness measurements. For the gravimetry, the most problematic point is that the oxide scale thickness of the Si-face and the C-face cannot be distinguished. And for the ellipsometry, the method that uses interpretation of the reflected laser beam off the substances with modeling, the random distribution of these crystalline oxide scales, which have different refractive indexes from the amorphous oxide scale, will lead to a level of inaccuracy in thickness measurement. Accordingly, it is crucial to specify the regions in which the thickness of the oxide scale will be measured in order to get accurate thickness measurements of the formed oxide scales.

In this study, we accurately measured the oxidation rates for the Si-face and the C-face of single crystal SiC by direct thickness measurement of the oxide scale specifically from the regions composed of only amorphous phase silica using electron microscopy. And in order to minimize the effect of other parameters on oxidation kinetics, such as contaminations or water vapor, the experimental procedures were designed and controlled accordingly. A high quality single crystal 6H-SiC wafer was used for samples in the oxidation experiments. The samples were oxidized in pure oxygen in an environment where the contamination level was minimal.

2. Experimental procedures

The single crystal n-type 6H-SiC wafer used in this study was provided by Cree Inc. The wafer was polished by chemical mechanical polishing (CMP) on both the Si-face and the C-face. The wafer was cut into $10 \times 10 \text{mm}^2$ size pieces and rinsed successively in acetone and ethanol. The samples were then loaded onto a quartz sample holder and put into the quartz tube furnace. The quartz sample holder and the quartz furnace tube were cleaned in HF prior to the oxidation experiments. The use of a quartz sample holder and furnace tube was to minimize the effects on oxidation from contaminations as reported in the case of alumina furnace tubes. Flowing 99.999 percent oxygen was introduced for 2 h prior to the oxidation to ensure a pure oxygen environment. The furnace system was then heated up at the rate of 10 degrees/min. The oxidation condition was 1273–1473 K from 1 to 25 h in flowing oxygen at 1 atm.

The oxidized samples were then observed using OM to identify the regions where the oxide scales were composed of only the uniformly formed amorphous silica. Then, platinum was deposited on the surfaces of the samples to prevent electrical charging. After carbon and tungsten deposition to protect the surface of the specimens, cross-sectional SEM or TEM specimens were prepared from regions where the oxide scales were composed of only the uniformly formed amorphous silica as determined by the FIB micro-sampling technique using a HITACHI NB-5000 FIB-SEM system. Thicknesses of the thermally formed oxide scales were measured using the SEM at an accelerating voltage of 5 kV. However, in the cases where the formed oxide scales were thinner than 100 nm, the measurements were conducted directly using a TEM, JEM-2010 at an accelerating voltage of 200 kV.

3. Results

The thickness of the oxide scales was measured over an approximately 20 micrometers range for each sample, i.e., the width of the TEM specimens, and the average thickness of each sample from each oxidation condition was obtained from 20 measurement points. Figures 2(a)–2(c) show the cross-sectional TEM images of the Si-face of the samples oxidized at 1273, 1373 and 1473 K for 1 h, respectively. The average thicknesses of each of the formed oxide scales were 6, 14 and 41 nm, respectively. Figures 3(a)–3(c) show the cross-sectional TEM images of the C-face of the samples oxidized at 1273, 1373 and 1473 K for 1 h, respectively. The average thicknesses of the oxide scales were 38, 81 and 151 nm, respectively. All TEM specimens were taken from the regions without glossy patterns. The oxide scales were uniformly formed and composed of only amorphous silica. For the same oxidation time and temperature, the oxide scale formed on the C-face was thicker than that of the Si-face. This agrees well with previous studies, which reported that the C-face oxidizes 3–10 times faster than that of the Si-face.

Figures 4(a) and 4(b) show oxide thickness as a function of time for each oxidation temperature for the Si-face and the C-face, respectively. The error bars are shown on each thickness data points in the figure.

4. Discussion

A model developed by Deal and Grove has often been used to describe the oxidation of SiC. This model was originally developed for the oxidation of silicon, but it also can be applied...
effectively to the oxidation of SiC. The model describes a general linear-parabolic relationship between the thickness of the formed oxide scale and the oxidation time as described in Eq. (1);

\[ X^2 + AX = B(t + \tau) \]  

(1)

Where, \( X \) is the thickness of the oxide scale, \( t \) is the oxidation time and \( \tau \) is the constant related to the initial thickness of the oxide scale prior to the oxidation. \( B/A \) and \( B \) are referred to as the linear rate constant and the parabolic rate constant, respectively.

We fit our experimental data to the Deal–Grove model to determine the rate constants for each oxidation temperature. The fittings of the Deal–Grove model are shown as solid lines in Figs. 4(a) and 4(b). The parabolic rate constants \( B \) derived from the fittings and the correlation coefficient, \( R^2 \), are shown in Table 1. The value of the correlation coefficient, which varies from 0 to 1, gets closer to 1 if the experimental data fits well with the model. From the \( R^2 \) value shown in Table 1, it can be concluded that our experimental data fit well with the Deal–Grove model.

Using the Arrhenius equation \([\text{Eq. (2)}]\), we determined the oxidation activation energy for the Si-face and the C-face.

\[ K = F \exp\left(-\frac{E_a}{k_B T}\right) \]  

(2)

Where, \( K \) is temperature dependent time constant, \( F \) is pre-exponential factor, \( E_a \) is the activation energy, \( k_B \) is the Boltzmann constant and \( T \) is the oxidation temperature.

The Arrhenius plot of the parabolic rate constants derived from the thickness measurements obtained in our study is shown in Fig. 5. From the slope of the plots, putting the parabolic rate constants \( B \) into \( K \) in Eq. (2), we determined the activation energies \( E_{\text{ap}} \) of \( B \) for the Si-face to be 358 kJ/mol and the C-face to be 85 kJ/mol.

The linear rate constants \( B/A \) derived from the fittings are shown in Table 2. The Arrhenius plot of the linear rate con-
However, there is the difficulty to explain the difference in diffusion of the oxygen as well as CO which take place both in the oxide layer with the identically same microstructure on both the Si- and C-face as reported in our previous works. This high activation energy may be not only due to the outer-diffusion coefficient of CO in the vitreous silica as the rate controlling step but also due to the temperature dependence of chemical potential gradient and concentration of the rate controlling species, as the result of difference on interface reaction as mentioned by Song, et al., which could be a candidate of explanation. Moreover, the slightly poor fitting of oxide thickness measurements and the higher deviation of data points in the Arrhenius plot of $B/A$ as well as of $B$ for the Si-face could suggest that the phenomenon is not simply obeying the Deal–Grove model originally discussed by them in a constant rate controlling step but in the varying rate controlling step with temperature. The existence of impurity Ca which showed the diffusion and aggregation during oxidation has been reported. If the aggregation of the impurity took place not only in the vitreous silica but also on the SiC/silica interface during oxidation, this process could affect the variation of the rate controlling step.

For the C-face, the activation energy obtained for the parabolic rate constant is close to what is reported for the diffusion of oxygen molecule in vitreous silica. This indicates that oxygen diffusion should be the rate controlling step as suggested by Ramberg and Worrell. Our result for the activation energy is slightly lower than the standard value of high purity silica. Impurities could cause the lower activation energy as they also suggested. Similar lower values of activation energy have been reported for fused silica, which is, possibly, due to impurities. In our research, we have minimized the impurities. However, the existence of residual Ca has been found in some detailed microstructural studies. This could be responsible for the low activation energy. Compared to the lower value of the activation energy for the parabolic rate constant $B$, the higher activation energy has been derived from the linear rate constants $B/A$ for the C-face among the other reported values. This higher value compared to the other study could also be affected by the impurity effect on the interface reaction at the SiC/silica interface. Further study should be required particularly on the interface structure during reaction to understand the activation energy for the linear rate constant $B/A$. However, the extraordinarily low deviation in the Arrhenius plots of $B/A$ as well as of $B$ suggests that the Deal–Grove model with a constant rate controlling step is well applicable to the oxidation of the C-face more than Si-face.

The higher activation energy of the parabolic rate constants $B$ in the other research could be understood as the result of devitrification of the oxide layer. The devitrification will affect not only the results of the thickness measurement but also the mechanism of oxidation.

In ellipsometry, a detailed structure of the sample must be known in order to interpret the ellipsometric data. The devitrification will change the morphology of the surface, i.e., surface roughening as shown in Fig. 1(c), as well as the refractive index of the oxide layers. These will produce inaccuracy in the measurement.

Besides the complication of measurement using ellipsometry when devitrification is involved, the diffusion of oxidants in amorphous silica and in crystalline silica must also be considered. The diffusion rate of oxygen in cristobalite was reported as lower than in amorphous silica.

### Table 2. The linear rate constants $B/A$ derived from the fittings of the Deal–Grove model to Figs. 4(a) and 4(b)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$B/A$ (nm$^2$/h$^2$)</th>
<th>$B/A$ (nm$^2$/h$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si-face</td>
<td>C-face</td>
</tr>
<tr>
<td>1273</td>
<td>1.583</td>
<td>35.07</td>
</tr>
<tr>
<td>1373</td>
<td>21.58</td>
<td>364.6</td>
</tr>
<tr>
<td>1473</td>
<td>28.08</td>
<td>3374</td>
</tr>
</tbody>
</table>

![Fig. 6. Arrhenius plot of linear rate constants.](image)

### Table 3. The oxidation activation energy of the Si-face and the C-face from previous studies and this study

<table>
<thead>
<tr>
<th>Reference</th>
<th>$E_{al}$ (kJ/mol)</th>
<th>$E_{al}$ (kJ/mol)</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>356</td>
<td>197</td>
<td>970–1245</td>
</tr>
<tr>
<td>7)</td>
<td>372</td>
<td>134–197</td>
<td>1200–1500</td>
</tr>
<tr>
<td>4)</td>
<td>292</td>
<td>99.3</td>
<td>800–1100</td>
</tr>
<tr>
<td>19)</td>
<td>240</td>
<td>120–202</td>
<td>1200–1500</td>
</tr>
<tr>
<td>12)</td>
<td>300.9</td>
<td>129</td>
<td>950–1150</td>
</tr>
<tr>
<td>This study</td>
<td>358</td>
<td>228</td>
<td>1000–1200</td>
</tr>
</tbody>
</table>
On the other hand, the devitrification will cause local volume change and, consequently, the formation of a crack in the oxide layer, which could be the shortcut for oxygen passage, exposing the SiC surface directly to the gaseous phase. This result suggests a possible mechanism for the coexistence of the two simultaneous rate controlling processes: the interfacial or surface reaction controlled one and the diffusion process controlled one. This situation would cause a deviation from the Deal–Grove model and result in a higher activation energy value for the parabolic rate constant. This suggests a reason for the higher activation energies, compared to our results, determined by other investigators who were using comparable or thicker oxide layer thicknesses.

Our results which are obtained from the oxide scales in the regions composed of only amorphous silica are free from the above mentioned difficulty in contrast to the other studies, which did not specify the regions where oxide scale thickness measurement were conducted. If this is the case, the lack of difference in the activation energy for the Si-face also implies that the devitrification rate of the oxide scale on the C-face has progressed more than on the Si-face. It was reported that the C-face has higher surface roughness compared to the Si-face. This supports the implication that the C-face devitrifies more than the Si-face.

We believe that our results of thickness measurements from the doubtless single amorphous phase oxide layer strongly confirm the rate controlling process of C-face oxidation as the oxygen diffusion in silica, and precise phase specific measurement of the thickness of the oxide layer should be required for a true understanding of the oxidation mechanism of SiC.

5. Summary

The thermally formed oxide scales on single crystal hexagonal silicon carbide were investigated using OM, SEM and TEM. Crystalline oxide scales were found randomly distributed on both the Si- and the C-face of the oxidized samples. For accurate thickness measurement, FIB micro-sampling technique was applied to prepare samples for measurement of the thermally formed oxide scales from the amorphous silica regions. The thickness of the oxide scales was measured directly using SEM and TEM. The oxidation activation energy for the parabolic rate constant obtained from the amorphous silica layer was found to be 358 kJ/mol for the Si-face and 85 kJ/mol for the C-face. The results obtained strongly suggest that the rate controlling process of the C-face oxidation is the diffusion of oxygen in the oxide layer.

References