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Kinetics of Thermal Oxidation of 6H Silicon Carbide in Oxygen Plus Trichloroethylene

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In this work, the behaviors of the trichloroethylene (TCE) thermal oxidation of 6H silicon carbide (SiC) are investigated. The oxide growth of 6H SiC under different TCE concentrations (ratios of TCE to O_2) follows the linear-parabolic oxidation law derived for silicon oxidation by Deal and Grove, *J. Appl. Phys.*, **36** (1965). The oxidation rate with TCE is much higher than that without TCE and strongly depends on the TCE ratio in addition to oxidation temperature and oxidation time. The increase in oxidation rate induced by TCE is between 2.7 and 67% for a TCE ratio of 0.001-0.2 and a temperature of 1000-1150°C. Generally, the oxidation rate increases quickly with the TCE ratio for a TCE ratio less than 0.05 and then gradually saturates for a ratio larger than 0.05. The activation energy $E_{B/A}$ of the TCE oxidation for the TCE ratio range of 0.001-0.2 is 1.04-1.05 eV, which is a little larger than the 1.02 eV of dry oxidation. A two-step model for the TCE oxidation is also proposed to explain the experimental results. The model points out that in the SiC oxidation with TCE, the products (H_2O and Cl_2) of the reaction between TCE and O_2 can speed up the oxidation, and hence, the oxidation rate is highly sensitive to the TCE ratio.
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In recent years, SiC has been an attractive wide-bandgap semiconductor material for high-temperature, high-frequency, and high-power applications.[1] SiC-based metal oxide semiconductor field-effect transistors (MOSFETs) and other MOS-related structures are promising devices for these purposes.[2] Because the high-quality gate insulator plays a critical role in MOSFETs, many researchers have studied the kinetics of SiC oxidation and the effects of oxidation method on the performance of SiC oxide films.[3-18] The methods of wet oxidation, dry oxidation, N_2O oxidation, NO oxidation, and NH_3 nitridation, commonly used for silicon, have been investigated for SiC. However, trichloroethylene (TCE) oxidation is also a popular method for oxidizing silicon and has been shown to improve the performance and electrical properties of the oxide film.[19,20] Compared to HCl, TCE is much easier to handle, because it is far less corrosive. As a result, TCE is widely used for cleaning the quartz tubes of oxidation furnaces and fabricating gate-oxide films in the semiconductor industry. However, the TCE oxidation method is not yet fully studied for SiC, although preliminary work demonstrated that it can also enhance the quality of the SiO_2/SiC interface and reduce the thermal budget.[21] Therefore, this work focuses on the behaviors and kinetics of SiC thermal oxidation in the presence of TCE.

Experimental

The n-type (0001) Si-face 6H-SiC wafers used in this investigation were purchased from CREE Research, Inc. The wafers had a 5 μm epitaxial layer grown on a heavily doped substrate. The doping concentration of the epitaxial layer was 4×10^{15} cm^{-3}. The wafers were cleaned using the conventional RCA method followed by a 1 min dip in 5% HF solution[22] and then loaded into an oxidation furnace. The samples were divided into three temperature groups (1000, 1100, and 1150°C). The samples of each temperature group were oxidized in dry O_2 and TCE for 30, 90, 150, 210, and 330 min, respectively. The ratio of TCE to dry O_2 was 0, 0.001, 0.01, 0.05, 0.1, and 0.2. The TCE vapor was added to the oxidizing ambient by a gas controller, which consisted of a dry oxygen switch and a dry nitrogen switch. The amount of TCE was controlled by varying the flow rate of the dry nitrogen inlet through a bubbler filled with purified liquid TCE and kept at 0°C. After the wafers were oxidized, their oxide thicknesses and refractive indices were measured by a variable angle spectroscopic ellipsometer series ellipsometer of J. A. Wollam Co., Inc. with an error of 0.5 to 3% for the oxide thicknesses.

Table I shows the refractive indices of the samples at a wavelength of 540 nm. The refractive indices agree with the theoretical

value of SiO_2 (1.46). Therefore, the oxide grown with O_2 and TCE on SiC should be SiO_2. This can be further supported by the fact that the oxide can be easily etched away by HF solution. No clear dependence of the refractive index on TCE ratio, oxidation temperature, and time can be observed.

Results and Discussion

Dependence of oxide thickness on oxidation time.—It has been reported[23-25] that the dependence of oxide thickness on oxidation time for the thermal oxidation of SiC can be described by a linear-parabolic oxidation law, as derived for silicon oxidation[26]

$$x^2 + Ax = B(t + \tau) \qquad [1]$$

where x is the oxide thickness and t the oxidation time. The quantity τ accounts for the presence of an oxide layer before the oxidation, and A and B are constants.

For short oxidation times, Eq. 1 can be approximated by

$$x \cong B/A(t + \tau) \qquad [2]$$

B/A is called the linear rate constant and is proportional to the chemical reaction rate at the wafer surface. The oxide growth rate is constant and independent of the oxide thickness because the process is limited by the surface reaction of SiC only. For long oxidation times, the oxide thickness is approximately governed by

$$x^2 \cong Bt \qquad [3]$$

where B is called the parabolic rate constant. Because the diffusion of oxidizing species through the oxide layer becomes the limiting process, the growth rate is controlled by the oxide thickness.

Figure 1 shows the dependence of oxide thickness on oxidation time under different TCE ratios for 1000, 1100, and 1150°C. For the same temperature and time, the oxide thickness for oxidation with TCE is much larger than that without TCE. Moreover, for different TCE ratios, the oxidation rate is enhanced by different extents. This is discussed later. However, the thermal oxidations with different TCE ratios all have a behavior similar to the dry O_2 oxidation, and thus the oxide growth of SiC in TCE and dry O_2 also observes the linear-parabolic oxidation law given in Eq. 1.

Assuming that the rate constants obey Arrhenius's law, B/A and B can be expressed as[27]

$$B/A = C_1 \exp(- E_{B/A}/kT) \qquad [4]$$

$$B = C_2 \exp(- E_B/kT) \qquad [5]$$

where C_1 and C_2 are pre-exponential constants. C_1 depends on the oxidation ambient and substrate orientation, whereas C_2 depends only on the ambient. k is the Boltzmann constant. $E_{B/A}$ and E_B are the activation energies for B/A and B, respectively.

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Table I. Refractive indices of samples at wavelength of 540 nm.

| Oxidation temperature (°C)	(TCE/N_2):O_2	Refractive index for different oxidation times				
		30 min	90 min	150 min	210 min	330 min
1000	0	1.46	1.48	1.48	1.48	1.48
	0.01	1.46	1.46	1.47	1.47	1.48
	0.2	1.46	1.46	1.47	1.46	1.47
1100	0	1.47	1.47	1.48	1.47	1.47
	0.01	1.48	1.46	1.46	1.47	1.47
	0.2	1.48	1.47	1.47	1.47	1.48
1150	0	1.47	1.47	1.47	1.47	1.46
	0.01	1.47	1.47	1.46	1.46	1.47
	0.2	1.46	1.46	1.46	1.46	1.46

Gölz *et al.* pointed out that for the Si-face thermal oxidation in pure dry O_2 ambient, after an initial accelerated oxidation, the oxide growth follows a linear law for up to 300 h in the temperature range of 1050-1200°C.[23] Therefore, assuming that the oxidation of all the samples follows the linear law in this investigation, $E_{B/A}$ can be extracted from the slope of the Arrhenius plot $\ln(B/A)$ *vs.* $1/T$. For the oxidation in pure dry O_2, $E_{B/A}$ is 1.02 eV, which is consistent with the result reported in Ref. 23. $E_{B/A}$ for oxidation with a TCE ratio in the range of 0.001-0.2 is 1.04-1.05 eV. Although $E_{B/A}$ is slightly increased by TCE, B/A is increased due to the larger value of C_1 induced by TCE.

Effects of TCE ratio on oxidation rate.—Figure 2 shows the dependence of the oxide thickness on the TCE ratio for different oxidation temperatures and times in SiC oxidation. When the TCE ratio is less than 0.05, the oxide thickness increases quickly with the ratio. For larger TCE ratios, it tends to saturate.

To clearly analyze the effect of TCE ratio on the oxidation of SiC, the oxidation rates of all the samples for different temperatures and times are calculated and plotted in Fig. 3. The oxidation rate strongly depends on the TCE ratio, in addition to oxidation temperature and time. For the shorter oxidation time (30 min), the oxidation rate increases quickly with the TCE ratio for TCE ratio less than 0.05 and then increases slowly for larger ratios. For longer oxidation times (150 and 330 min), the oxidation rate increases with the TCE ratio for a ratio less than 0.05 and tends to saturate gradually for ratios larger than 0.05. Furthermore, observe that, under the same temperature, the oxidation rate for the shorter oxidation time is higher than that for the longer oxidation time, supporting the linear-parabolic oxidation law.

The increase of oxidation rate induced by TCE depends on the TCE ratio, oxidation temperature, and time. Based on the experimental data, it is calculated to be between 2.7 and 67% for a TCE ratio of 0.001-0.2 and a temperature of 1000-1150°C. Therefore, to obtain a higher oxidation rate, the TCE ratio for SiC thermal oxidation should be within 0.01-0.1 for 1000-1150°C. However, the effects of TCE ratio on the electrical properties of the oxide films are another concern, and must be considered in determining the optimal oxidation conditions.

Oxidation model.—The process of SiC thermal oxidation can be divided into two steps.[28,29] First, the oxidation of the SiC surface occurs through the insertion of an oxygen atom into the chemical bond of a SiC molecule. This oxygen insertion creates an Si — O — C species, which then splits into a CO molecule and an Si atom with a dangling bond. The CO molecule then diffuses through the oxide to the oxide surface and reacts with an oxygen atom, creating CO_2. Second, the Si atom reacts with oxygen atoms, which are at the SiC surface in the initial oxidation or diffuse through the oxide to the oxide-SiC interface, forming SiO_2. These two processes can be summarized by the following reactions

$$SiC + O \rightarrow CO_2 + Si \qquad [6]$$
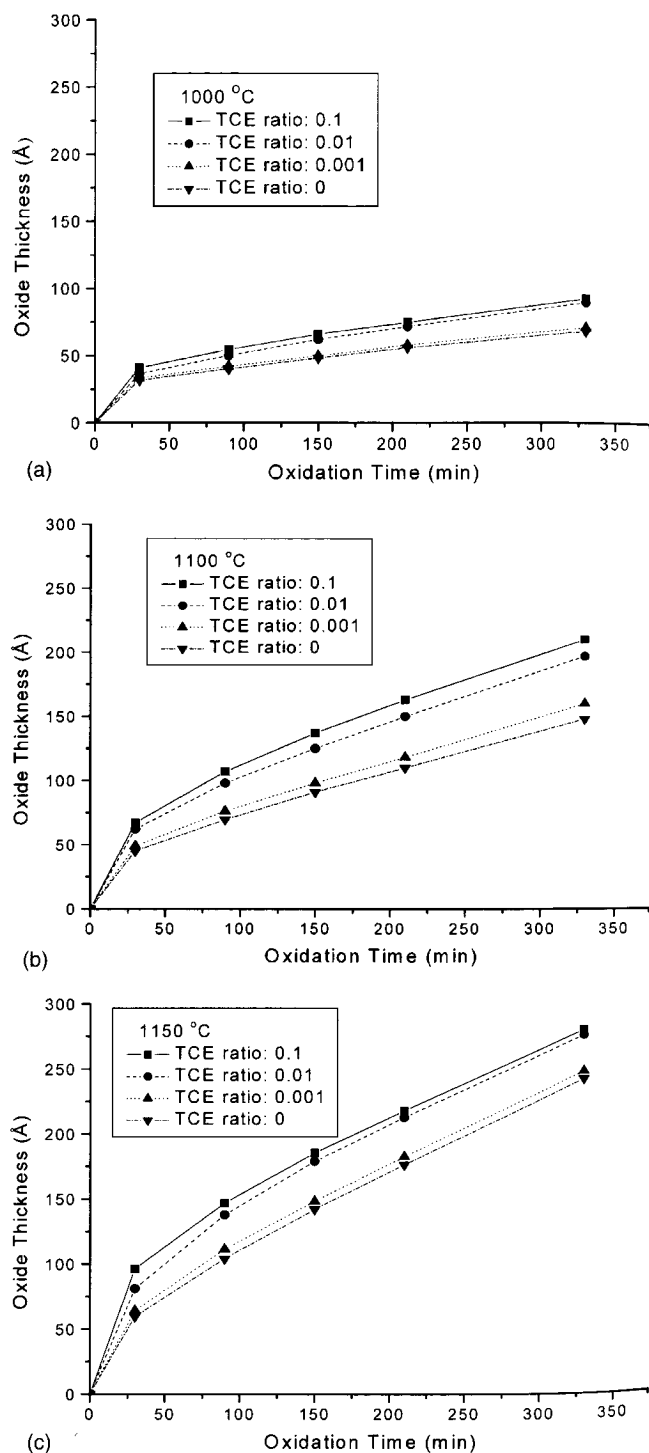
Figure 1. Dependence of oxide thickness on oxidation time for different TCE ratios at (a) 1000, (b) 1100, and (c) 1150°C.

$$Si + 2O \rightarrow SiO_2 \qquad [7]$$

Because the SiC thermal oxidation must go through the first step, and the bond breakage to extract CO from the SiC subsurface is slow, SiC oxidation is slower than Si oxidation under the same process conditions. The fact that SiC oxidation finally involves an Si oxidation step provides an explanation for SiC oxidation also observing the linear-parabolic oxidation law as Si oxidation.

For the TCE oxidation in this work, TCE with a chemical composition of C_2HCl_3 can react with O_2

Figure 3. Dependence of oxidation rate of SiC on TCE ratio, oxidation temperature, and time.

(H_2O and Cl_2) of the reaction between TCE and O_2 can also speed up the second step of the oxidation process. As a result, Fig. 3 shows that the oxidation rate with TCE is higher than that with pure dry O_2. Because the equilibrium concentrations of H_2O and Cl_2 in the TCE/O_2 system depend on the system temperature and TCE ratio,[30] the increase of oxidation rate varies with the TCE ratio, oxidation temperature, and time. However, the SiC oxidation with TCE is a complex chemical process; thus, its detailed physical mechanisms for the oxidation kinetics still require further investigations.

Conclusion

The behaviors of TCE thermal oxidation of 6H-SiC have been investigated. Experimental results show that the oxide growth under different TCE ratios follows the linear-parabolic oxidation law as in silicon oxidation. The oxidation rate with TCE is much higher than that with dry O_2 only and depends strongly on the TCE ratio, in addition to oxidation temperature and time. The increase of oxidation rate induced by TCE is between 2.7 and 67% for a TCE ratio of 0.001-0.2 and a temperature of 1000-1150°C. In general, the oxidation rate increases quickly with the TCE ratio for TCE ratio less than 0.05, and then slowly saturates for larger ratios. The activation energy $E_{B/A}$ of the oxidation with TCE ratio in the range of 0.001-0.2 is 1.04-1.05 eV. Moreover, a two-step model is proposed for the TCE oxidation of SiC. The model points out that the by-products (H_2O and Cl_2) of the reaction between TCE and O_2 can speed up the thermal oxidation; thus, the oxidation rate strongly depends on the TCE ratio.

Acknowledgments

Figure 2. Dependence of oxide thickness on TCE ratio and temperature for (a) 30, (b) 150, and (c) 330 min.

$$4C_2HCl_3 + 9O_2 \rightarrow 8CO_2 + 2H_2O + 6Cl_2 \qquad [8]$$

$$2H_2O + 2Cl_2 \rightleftharpoons 4HCl + O_2 \qquad [9]$$
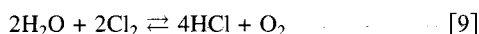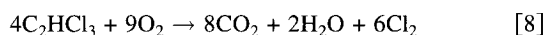
It has been reported that in the silicon thermal oxidation with TCE, the by-products H_2O and Cl_2 can increase the silicon oxidation rate.[30] The addition of water from 0 to 2000 ppm to the dry O_2 ambient can significantly enhance the oxidation rate. Also, for an additive chlorine concentration of 0.16-0.87%, a relatively large increase in the oxidation rate has been observed. Therefore, one can suggest that in the SiC oxidation with TCE, the by-products
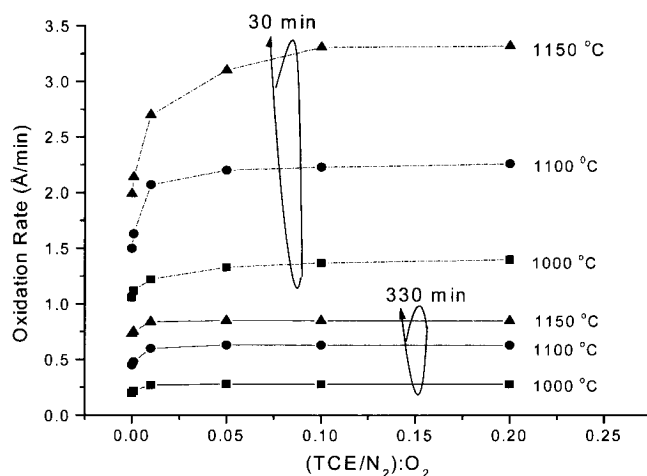
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