# Kinetics of Enhanced Oxide Growth on 4H-SiC in O2 and H2O Coexisting Ambient

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## Abstract

We investigated the kinetics of 4H-SiC (0001) wet oxidation from the viewpoints of the oxidation temperature and oxidizing ambient ( $O_2$  and  $H_2O$ ) composition dependence. It was found the coexistence of  $O_2$  and  $H_2O$  enhanced oxidation rate and the activation energy becomes smaller as compared with the case of oxidation by  $O_2$  or  $H_2O$  only. It is indicated that oxidation mechanism of coexistence mode is different from that of  $O_2$  or  $H_2O$  single mode oxidation.

## 1. Introduction

It is well known that the interface property of  $SiC/SiO_2$  varies depending on the oxidation method, and that a significant difference appears between dry and wet oxidation in particular. But the reason of such difference has not been clarified yet. In addition, oxidation rate differs greatly between dry and wet oxidation [1], but systematic investigation has not been done so far. In this study, we investigated the oxide growth rate on SiC surface in the reaction-limited mode for the thermal oxidation only with H<sub>2</sub>O and that with two coexisting oxidants O<sub>2</sub> and H<sub>2</sub>O, to discuss the characteristics of the oxidation mechanisms.

## 2. Experimental Method

Wet oxidation was carried out on  $4^{\circ}$  off n-type 4H-SiC (0001) and (000-1) wafers in the ambient prepared by bubbling method by flowing N<sub>2</sub> or O<sub>2</sub> gas through deionized water whose temperature was controlled (hereafter wet-N<sub>2</sub> and wet-O<sub>2</sub>, respectively). The growth temperature dependence and oxidizing species dependence of oxidation rate were investigated. The film thickness was accurately determined by grazing incidence x-ray reflectivity (GIXR). **Fig.1** is typical experimental data and simulation results of GIXR.

#### 3. Result and Discussion

The relationship between oxidation time and oxide thickness for the case of wet-N<sub>2</sub> oxidation, at each temperature is shown in **Fig. 2**. The almost linear relationship indicates that the oxidation in this region occurs in the interface reaction-limiting mode. The oxidation rate was determined from the slope in linear region in the thickness range of 2 to 28 nm for Si-face samples.

For wet-O<sub>2</sub> oxidation at 1100°C, the relationship between oxidation rate and pH<sub>2</sub>O ratio in oxidizing species (pH<sub>2</sub>O/(pO<sub>2</sub>+pH<sub>2</sub>O)) is shown in **Fig. 3(a)**, together with the data of dry-O<sub>2</sub> [2] and wet-N<sub>2</sub> at both ends. When O<sub>2</sub> and H<sub>2</sub>O

coexisted even slightly with each other, the oxidation rate significantly increased. No large change was observed when H<sub>2</sub>O ratio was in the range of 0.4 to 0.9, but the rate was several times faster than that of O<sub>2</sub> or H<sub>2</sub>O alone. From this result, it is indicated that a new oxidation mechanism appears under the coexistence of O<sub>2</sub> and H<sub>2</sub>O, which is quite different from oxidation in the case where each of them exists alone, as schematically shown in **Fig. 3(b)**. This behavior will be a characteristic phenomenon for SiC oxidation, because such dependence on pH<sub>2</sub>O is not observed in wet oxidation of Si wafer [3], where the growth rate monotonically increases with pH<sub>2</sub>O.

The temperature dependence of the oxidation rates in wet-N<sub>2</sub> (pH<sub>2</sub>O~0.9 atm) and wet-O<sub>2</sub> (0.6 atm) is shown in **Fig. 4**, together with their activation energies,  $E_a$ . The data of dry-O<sub>2</sub> oxidation [2] are also shown as broken line. For the temperature range from 1000°C to 1150°C, the oxidation rate of wet-N<sub>2</sub> was similar to that of dry-O<sub>2</sub>. Considering that these oxidations are in the interface reaction-limiting mode and that



Fig 1. Typical experimental data and simulation results of GIXR. The film thickness and density of two examples are obtained from the fitting as indicated. SiO<sub>2</sub> single layer was assumed in calculation



Fig. 2. Relationship between grown oxide thickness and oxidation time for different oxidation temperatures, for the wet-N<sub>2</sub> oxidation on Si-face with  $pH_2O\sim0.9atm$ . The rate constant in interface reaction-limited at each temperature is indicated.



Fig. 3. (a) Dependence of oxidation rate on composition of oxidizing ambient (O<sub>2</sub> and H<sub>2</sub>O). A characteristic oxidation mode with faster oxidation rate appears under coexistence of comparable O<sub>2</sub> and H<sub>2</sub>O partial pressure. (b) Schematic image of oxidations by (I) O<sub>2</sub>, (II) O<sub>2</sub>+H<sub>2</sub>O, (II) H<sub>2</sub>O. In (II) oxidation, the reaction is significantly enhanced compared to (I) or (II).

the dissolved amount of oxidizing species in  $SiO_2$  is two-orders larger for  $H_2O$  than  $O_2$  [4], the rate constant of SiC interface reaction with  $H_2O$  should be much smaller than that with  $O_2$ .

The observed activation energy,  $E_a$  of wet-O<sub>2</sub> was ~1.5 eV, which is smaller than that of either dry-O<sub>2</sub> or wet-N<sub>2</sub> oxidation. As a result, the difference in oxidation rates is more pronounced at lower temperature. The reason for the observed enhancement even with only 10% O<sub>2</sub> addition to wet ambient is explainable that the reaction with small  $E_a$  is dominant in such a composition region.



Fig. 4. The Arrhenius plot for oxide growth rate on Si-face in wet-N<sub>2</sub> ( $pH_2O\sim0.9$  atm) or wet-O<sub>2</sub> (0.6 atm) ambient. Broken line indicates that of dry-O<sub>2</sub>[2]. Activation energies are different for two types of wet oxidation processes, and the rate difference becomes larger at lower temperature.



Fig. 5. The comparison of the oxide growth rates on Si-face and C-face for the wet-O<sub>2</sub> ( $pH_2O\sim0.6$  atm) oxidation. There is about 10-times difference depending on the surface orientation.

Finally, for comparisons, we examined the oxidation kinetics on C-face for some conditions. It is well known that the dry-O<sub>2</sub> oxidation on C-face shows faster growth rate and lower activation energy. For example, the rate on C-face is about 10 times faster than that on Si-face at around 950°C [5]. A similar trend with our results on  $pH_2O/(pO_2+pH_2O)$  dependence shown in Fig. 3 has been already suggested for Cface in literature [6], that the addition of  $O_2$  in wet ambient significantly enhances the oxidation rate on C-face. Fig. 5 shows our data that the oxidation rate of wet-O2 on C-face was about 10 times faster than that on Si-face. Considering that the ratio of the growth rate on C-face to that on Si-face is close to that for the case of dry oxidation, it would be reasonable that the enhancement of oxidation rate under coexistence of H<sub>2</sub>O and O<sub>2</sub> should be a common phenomenon on SiC surface irrespective of surface orientations.

## 4. Conclusion

In this study, we investigated the surface oxidation kinetics of 4H-SiC mainly on Si-face in wet-N<sub>2</sub> and wet-O<sub>2</sub>. The oxidation rate of wet-N<sub>2</sub> is similar to that of dry-O<sub>2</sub>. In the wet-O<sub>2</sub> oxidation, it was found that the oxidation rate increases compared to oxidation by O<sub>2</sub> only (dry) or H<sub>2</sub>O only (wet-N<sub>2</sub>). We also found that activation energy  $E_a$  of wet-O<sub>2</sub> is smaller than  $E_a$  of wet-N<sub>2</sub>. The results suggested that the oxidation mechanism of wet-O<sub>2</sub> is different from wet-N<sub>2</sub> and dry-O<sub>2</sub> oxidation.

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