

Si emission into the oxide layer during oxidation of silicon carbide

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Abstract. To verify the Si emission phenomenon during oxidation of SiC, the behavior of Si atoms was investigated using HfO₂/SiC structures. At low oxygen pressure, i.e. the oxidation condition predominant to active oxidation, Si emission into oxide layer and the growth of SiO₂ on the oxide surface were clearly observed by TOF-SIMS. On the other hand, the growth of SiO₂ on the surface was suppressed under an ordinary pressure. These results evidence the Si emission during oxidation that is proposed in the Si and C emission model.

Introduction

It is still a severe issue that the prospective low on-resistances from the material properties of SiC have not been provided from actually fabricated SiC-MOSFETs, especially for 4H-SiC. This deterioration in low-loss performance is probably due to the high oxide fixed charge or high interface state density (D_{it}) observed in CV characteristics of SiC MOS capacitors [1]. Since the characteristics of thermally grown oxide layers and oxide-SiC interfaces should be closely related to the growth mechanism of oxide, further understanding of the oxidation mechanism of SiC is believed to be very significant.

We proposed a SiC oxidation model, termed ‘Si and C emission model [2].’ In the model, we assumed that Si and C atoms emit from the SiO₂/SiC interface into the SiO₂ layer during oxidation and the interfacial oxidation rate reduces if these atoms accumulate near the interface. We calculated growth rates using the Si and C emission model and, as a result, the calculated growth rate curves exactly reproduced the observed ones at the entire oxide thickness region [2–4]. However, the validity of this model is still doubtful because the direct observation of Si emission has not succeeded. On the other hand, C emission has been observed both of SiO₂ [5] and SiC substrate sides [6].

It has been reported that C injection into SiO₂ layer is attributed to the interface trap at wide energy range [7], or that the injected C interstitials into SiC create C dimers/di-interstitials in SiC layer, which gives rise to D_{it} near the conduction band-edge (E_c) [8,9]. Meanwhile, there are some reports that Si emission is the resource that causes the high D_{it} near E_c . Afanacev *et al.* found that such an interface trap, so-called near-interface-trap (NIT), is common in 6H-, 4H-SiC, and even in Si MOS capacitors [7]. Accordingly, they concluded that intrinsic defects in thermal oxidized SiO₂ such as strained interface are the origin of NITs. Dautricha *et al.* pointed out that Si vacancies in SiC bulk, which are probably due to the Si emission, are attributed to the NITs [10]. Anyway, it must be said that Si and/or C emission during oxidation is the key to elucidate the origin of interface trap of the SiO₂/SiC interface.

In this study, to directly observe the behavior of Si atoms during oxidation, we performed depth-profiling of the oxides after oxidation of HfO₂/SiC structures, as has been carried out for Si [11]. In addition, we compared the oxidation conditions that Si emission is predominance (i.e. *active oxidation* mode [12]) and that the interfacial oxide growth is predominance (i.e. *passive oxidation* mode). For the depth-profiling measurements, time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and angle-resolved X-ray photoelectron spectroscopy (AR-XPS) were employed.

Experiments

Figure 1 schematizes the concept of experiments in this study. When a whole of HfO₂/SiC structure is heated in an oxygen atmosphere, oxidants diffuse toward the HfO₂/SiC interface, and as a result of oxidation, Si atoms are emitted into the oxide layer. When the emitted Si atoms come across in-diffusing oxygen, a SiO₂ molecule is formed there. Therefore, SiO₂ is expected to grow at the oxide surface-side in the case of high oxidant diffusivity condition, i.e. low pressure and high temperature. The nature of HfO₂ is relatively close to that of SiO₂ in terms of IV-group oxide and its almost same bond-length. Accordingly, we employed a HfO₂ film to trace the locus of Si atoms instead of stable isotope SiO₂ film.

Epitaxial wafers of 4H-SiC with an 8° off-oriented (0001) Si-face, *n*-types, having a net donor concentration $N_d - N_a = 1 \times 10^{16} \text{ cm}^{-3}$ were used in this study. HfO₂ films of 5.6 nm thickness were grown by an electronic-beam evaporator. The surface roughness of grown HfO₂ films measured by an atomic force microscopy was within 0.4 nm, which is sufficient for TOF-SIMS analysis. The samples are oxidized for 1 and 10 min in an infrared-furnace of 1100°C in a dry stable-isotope oxygen (¹⁸O₂) atmosphere, aiming to trace the oxidant behavior under active oxidation condition. Note that a higher temperature and lower pressure leads to active oxidation predominance [13], and to passive oxidation predominance on reverse condition. Accordingly, we set the oxygen pressure down to 13 Pa to generate active oxidation mode. For comparison, a sample was annealed also in a high vacuum chamber (base pressure $< 1 \times 10^{-5} \text{ Pa}$) at 1100°C for 30 min. These samples were analyzed by TOF-SIMS using 25 keV Bi ion-species with a dose of $< 10^{12} \text{ cm}^{-2}$ and Cs⁺ ions as primary ions and sputter ions, respectively. The depths from the sample surface were given by assuming that the ion-etching rate was constant with respect to etching time and by measuring the depth of the crater formed by ion-etching.

Results and Discussion

Figure 2 shows the depth profiles of ¹⁸O, SiC, ¹⁷⁸Hf¹⁶O₂, Si₂¹⁸O₅ (equivalent to Si¹⁸O₂), and Si₃¹⁸O (equivalent to sub-oxide, i.e. Si¹⁺ in the reference [14]), for 1 min. oxidation (a) and 10 min. oxidation (b). The analysis for the annealed sample (not shown here) confirmed that no Si atom was emitted into the HfO₂ layer. On the other hand, the depth profiles in the case of oxidized samples clearly show that SiO₂ was grown near the HfO₂ surface. Besides, the SiO₂ growth in 10 min. oxidized sample proceeds more and the edge of SiO₂ at substrate-side is steeper than that of 1 min. These are strong indications that evidence the Si emission from the SiO₂/SiC interface into the SiO₂ layer during oxidation. Also these confirm that the emitted Si atoms out-diffuse toward the surface and are oxidized when they come across oxygen coming from the gas-phase. It is found that, under such an oxidation condition predominant to the active oxidation mode, a growth of SiO₂ at the interface hardly occurs and, instead, only sub-oxide grows between the surface SiO₂ layer and SiC substrate. In addition, the figure shows that the sub-oxide hardly increases with oxidation progress and that the sub-oxide is grown also near the SiO₂ surface (approx. 1 nm from the surface) though its amount is very small.

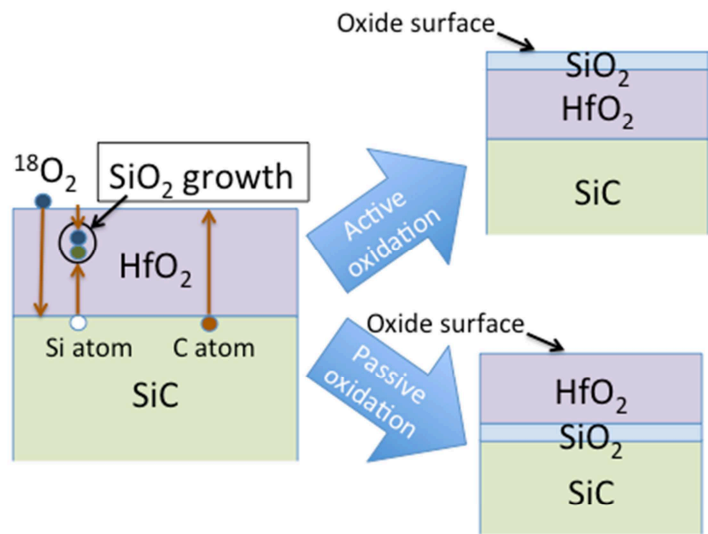


Fig.1. Schematic illustration of oxidation of HfO₂/SiC structure.

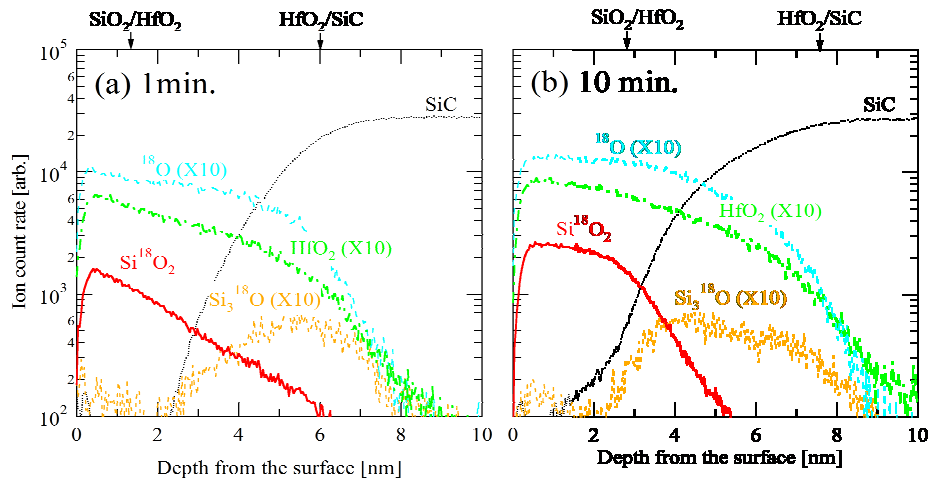


Fig. 2. Depth profiles of ¹⁸O, SiC, HfO₂, Si¹⁸O₂, and Si₃¹⁸O for 1 min. oxidation (a) and 10 min. oxidation (b).

As we expected, Si emission was clearly observed under active oxidation-predominant condition. Next, we examine the distribution of Si atoms in the case of passive oxidation-predominant condition. We analyzed depth-profile of the sample oxidized at ordinary pressure by AR-XPS.

Figure 3 shows O1s photoemission spectra at various photoelectron take-off angles for 1 min. oxidation (a) and 10 min. oxidation (b). The photoelectron take-off angle measures from the sample surface. The larger photoemission peak at lower energy-side (around 530 eV) originates from HfO₂. Another peak at higher energy-side (around 532 eV) originates from SiO₂. While SiO₂ peak slightly changes with take-off angle, HfO₂ peak significantly increases with increasing take-off angle. This shows the SiO₂ layer is located in the oxide surface side and the HfO₂ layer is located in SiC-side. It is therefore found that the active oxidation mode is still dominant despite ordinary pressure. Since the SiC peak in Si2p region was not strong enough, the thickness of SiO₂ could not be obtained from AR-XPS. Although spectroscopic ellipsometry did not determine an order of the oxide layers, it was determined that oxide consisted of HfO₂ of 4.8 nm and SiO₂ of 0.89 or 1.3 nm. Therefore, the oxide structure turned out to be SiO₂(0.89 nm and 1.3 nm)/HfO₂(4.8 nm)/SiC for 1 and 10 min. oxidation, respectively.

Next we consider oxide growth rates between 1 and 10 min. According to spectroscopic ellipsometry, the thicknesses of SiO₂ in the case of 13 Pa are 1.1 and 4.1 nm for 1 and 10 min., respectively. Therefore, the oxide growth rate during this term is 20 nm/h. For 1 atm, the growth rate is 2.7 nm/h, which is remarkably smaller than that for 13 Pa. This significant difference in growth rate also confirms the Si emission and diffusion in oxide.

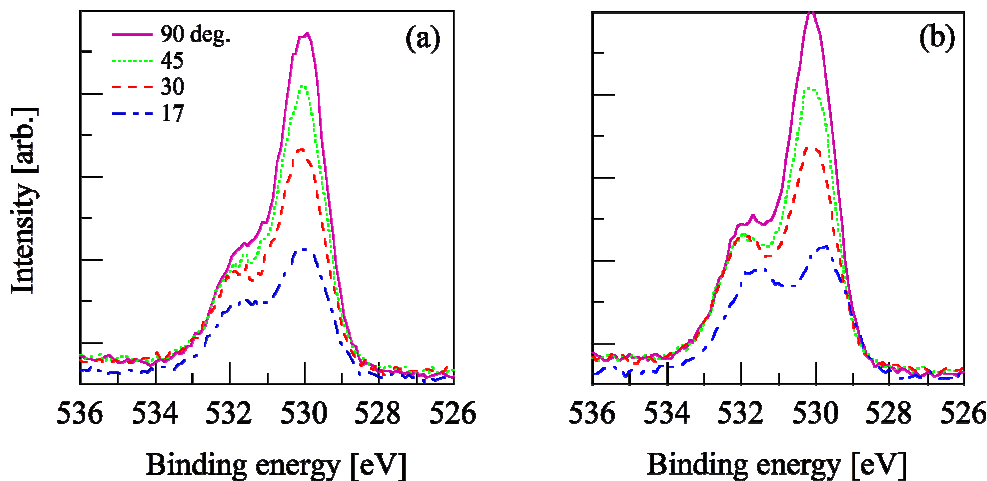


Fig. 3. O1s photoemission spectra at various photoelectron take-off angles for 1 min. oxidation (a) and 10 min. oxidation (b).

According to the previous work [13], the border between passive oxidation mode and active oxidation mode is around 0.1 atm because the oxidation rate at initial oxidation stage hardly depends on polar face in the case below this pressure. However, this work indicated that the active oxidation mode still remained at the range of oxide growth of around 1 nm. It is interesting that this thickness agrees with the upper limit of which an interface layer is scarcely formed [13,14]. Some articles have reported that the high temperature oxidation, i.e. active oxidation-predominant mode, gives rise to a high quality oxide film [15]. The reason for this may be attributable to surface oxide growth with rich oxygen and without strain in addition to an enhancement of C evaporation. We therefore believe that low-pressure oxidation is second choice of oxide improvement, as has been reported in Ref. [16].

Summary

The behavior of Si atoms during oxidation has been examined using HfO₂/SiC structures by TOF-SIMS. SIMS profiles for HfO₂/SiC structures oxidized under low-pressure stable-isotope oxygen, i.e. active oxidation condition, clearly exhibited the SiO₂ growth at the HfO₂ surface, which evidenced the Si emission into oxide during oxidation strongly. While in the case of ordinary pressure, AR-XPS profiles showed the SiO₂ growth at the HfO₂ surface was suppressed. It can be said that the knowledge acquired this time is very useful for the improvement of quality of an oxide film.

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