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Spectroscopic Observation of the Interface States at the SiO₂/4H-SiC(0001) Interface

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We obtained the energy distribution of the interface states at the SiO₂/4H-SiC(0001) interface using operando hard x-ray photoelectron spectroscopy. Two types of interface states were observed: one with continuous interface states in the entire SiC band-gap and the other with sharp interface states formed below the conduction band minimum (CBM). The continuous interface states in the whole gap were attributed to carbon clusters while the sharp interface states observed near the CBM were due to the Si₂-C=O state and/or the Si₂-C=C-Si₂ state at the SiO₂/SiC interface.

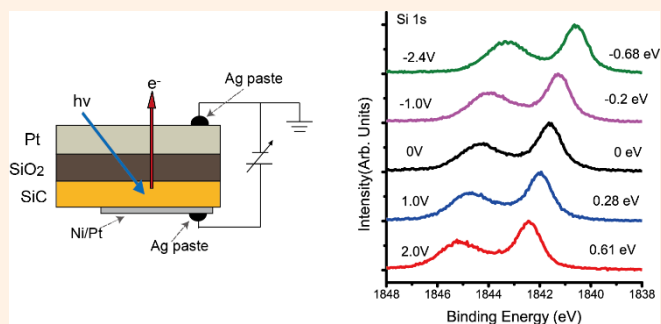
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I. INTRODUCTION

Silicon carbide (SiC) has recently attracted attention as a promising material for next-generation high-power high-frequency electronic devices [1]. One advantage of SiC for practical applications is the formation of insulating silicon oxide (SiO₂) layers on SiC by thermal oxidation [2–5]. However, the properties of the SiO₂/SiC interface are not well controlled, although they directly determine the electrical characteristic of a device [6–9]. One problem is that formation of a high density of interface states causes a poorer mobility than predicted.

For the SiO₂/SiC interface states, the energy distribution of the interface states at the SiO₂/SiC interface has yet to be obtained because deep interface states cannot respond to electrical signals due to their extremely large time constants. Once the origin of the interface states is clarified, it becomes possible to develop a method to reduce interface states, which could improve the development of SiC power device. Thus, a new method is needed to elucidate the energy distribution of the interface states in the whole SiC gap.

Recently, we developed a new spectroscopic method to observe the energy distribution of interface states based on operando hard x-ray photoelectron spectroscopy (OP-



HAXPES). That is, photoelectron spectroscopic measurements are conducted under a bias voltage application between a metal layer and a semiconductor substrate [10–12]. In the present study, this method is applied to the interface states at the SiO₂/SiC interface.

From the viewpoint of power device applications, 4H-SiC is most desirable due to the second largest band-gap among SiC polymorphism [13–16]. In this study, we investigated the energy distribution of the interface states at the SiO₂/4H-SiC(0001) interface using OP-HAXPES.

II. EXPERIMENTAL

We used a nitrogen-doped n-type SiC epitaxial layer (5- μm thick) with a donor density of $1 \times 10^{16} \text{ cm}^{-3}$ on the a 4H-SiC(0001) substrate (Nippon Steel & Sumikin Materials). The substrate was cleaned by the standard RCA method and dipped into a diluted HF solution. An 8-nm thick SiO₂ layer was formed by a heat treatment at 1200°C for 17 min in dry oxygen. Ohmic contact at the rear SiC surface was carried out by the deposition of a 100-nm thick Ni using a sputtering method and a subsequent heat treatment at 900°C in Ar for 30 min. Then 200-nm thick Pt was deposited by a sputtering procedure at RT. A 10-nm thick Pt layer was de-

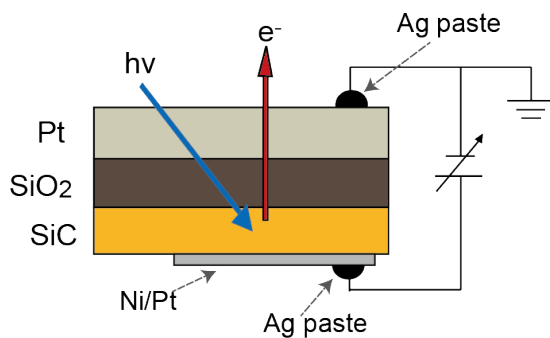


Figure 1: Schematic of the experimental setup for OP-HAXPES.

posited on the SiO₂ surface using the electron beam evaporation method.

For the OP-HAXPES measurements, a bias voltage was applied to the rear SiC while the topmost metal Pt layer was grounded. The OP-HAXPES measurements were performed using BL15XU at SPring-8 with an incident photon energy of 5.95 keV. A high energy version of VG SCIENTA R4000 analyzer was used as an electron analyzer. A total energy resolution was set to 240 meV for the OP-HAXPES measurements and to 170 meV for the standard HAXPES measurements [17]. Figure 1 schematically depicts the experimental setup for OP-HAXPES.

III. RESULTS AND DISCUSSION

Figure 2 shows the Si 1s spectra for the Pt/SiO₂/SiC structure as a function of the bias voltage. The peak observed at the lower binding energy is attributed to the SiC substrate peak, while the peak at the higher binding energy is due to SiO₂ [18]. Applying a positive bias voltage of 2.0 V

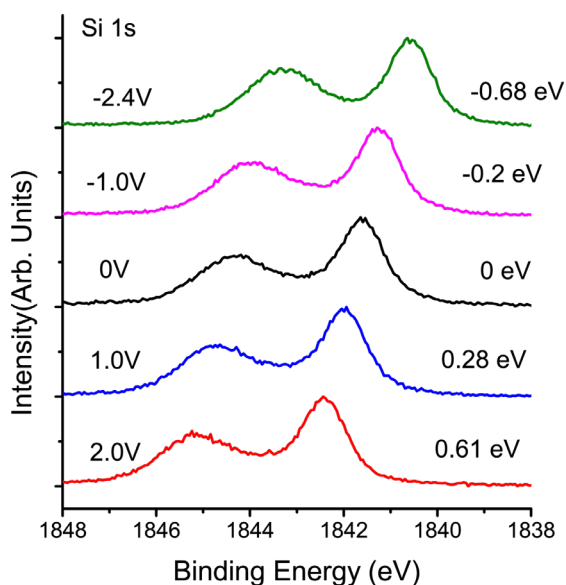


Figure 2: Bias-dependent Si 1s spectra for the SiO₂/4H-SiC(0001) structure as a function of the bias voltage. Each bias voltage was applied to SiC with respect to the Pt metal layer and the take-off angle was 88°.

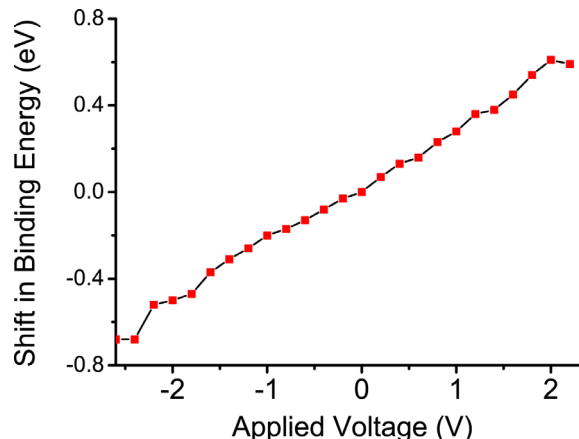


Figure 3: SiC substrate peak shift in the Si 1s region as a function of the bias voltage.

to SiC with respect to the Pt overlayer shifts the Si 1s substrate peak by 0.61 eV toward the higher binding energy. On the other hand, applying a bias voltage of -2.4 V shifts the substrate peak in Si 1s by -0.68 eV toward the lower binding energy. These bias-induced shifts are completely reversible; that is, the shift diminishes upon removing the bias voltage. Therefore, these shifts are attributed to the accumulation or release of charge in the electronic states by the bias. Moreover, when the quasi-Fermi level of the SiC substrate shifts upon a bias-voltage application, the Fermi level at the SiO₂/SiC interface is located at the same Fermi level as that of the SiC substrate because the structure does not exhibit a leakage current. Hence, we conclude that these shifts are due to the accumulation or release of charge at the SiO₂/SiC interface.

Figure 3 plots the peak energy shift of the SiC substrate in the Si 1s region as a function of the bias voltage. The slope of the plots confirms that the energy distribution of interface states can be obtained.

Figure 4 shows the energy distribution of the interface

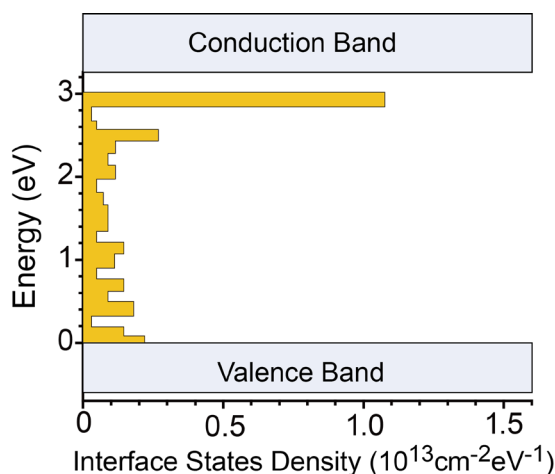


Figure 4: Energy distribution of the interface states at SiO₂/4H-SiC(0001) interface. Valence band maximum is set to the energy origin.

states for the SiO₂/4H-SiC(0001) interface. Note that the detailed principle to determine the interface states is described in our previous papers [10, 11, 19–21]. The energy distribution of the interface states is composed of two components: continuous interface states in the whole gap and sharp interface states near the CBM. The total density of the interface states is $4.58 \times 10^{12} \text{ cm}^{-2}$.

Figure 5 shows the C 1s and Si 1s spectra for a SiO₂/4H-SiC(0001) structure measured with different take off angles (TOAs). For the C1s spectra, the low binding energy peak is attributed to SiC, while the high binding energy peak is due to carbon clusters [22, 23]. Note that these peak positions are different from other articles [24, 25]. So far we have not clarified the reason. One possibility might be band-bending effect due to surface states and/or surface treatment [26].

To clarify the depth information of the carbon clusters, we compared the intensity ratio of each component at different TOAs. For TOA of 88° (bulk sensitive), the intensity ratios of C/SiO₂ and C/SiC are 0.079 and 0.084, respectively. For a TOA of 25° (surface sensitive), the intensity ratios of C/SiO₂ and C/SiC are 0.050 and 0.039, respectively. As shown in Figure 5, if the carbon clusters are located at the interface, the intensity increases as TOA increases. If the carbon clusters form uniformly in the SiO₂ layer, the intensity is independent of TOA. If the carbon clusters are located at the surface, the intensity decreases as TOA increases [27]. In the present study, the intensity ratios of C/SiO₂ and C/SiC increase as TOA increases. These results indicate that the carbon clusters are formed predominantly at the SiO₂/4H-SiC(0001) interface.

According to previous studies on the SiO₂/SiC interface, a carbon cluster at the interface exhibits interface states, where the energy levels depend on the cluster size. A small carbon cluster forms a bonding state and an anti-bonding state in the band-gap, and the energy difference depends on the cluster size [28]. Sufficient large clusters exhibit delocalized states, forming continuous interface states in the whole-gap [Figure 6(a)]. Therefore, we conclude that a large carbon cluster is responsible for the continuous interface states.

For the sharp interface states observed below CBM, the corresponding structure should be rigid due to the discrete energy level. Many studies have been performed on the interface states below CBM [29–32]. Among the structures proposed for the interface states below CBM, rigid structures for the interface states are limited to Si₂-C=O and Si₂-C=C-Si₂, which have planar structures [Figure 6(b, c)] [29]. Therefore, we propose that the sharp interface states observed below CBM are due to Si₂-C=O and/or Si₂-C=C-Si₂ states where structures are planar, although the possibilities of other structures cannot be excluded. Figure 6 summarizes the proposed interface state model.

IV. CONCLUSIONS

We observed the energy distribution of the interface states at the SiO₂/4H-SiC(0001) interface using OP-HAXPES. The

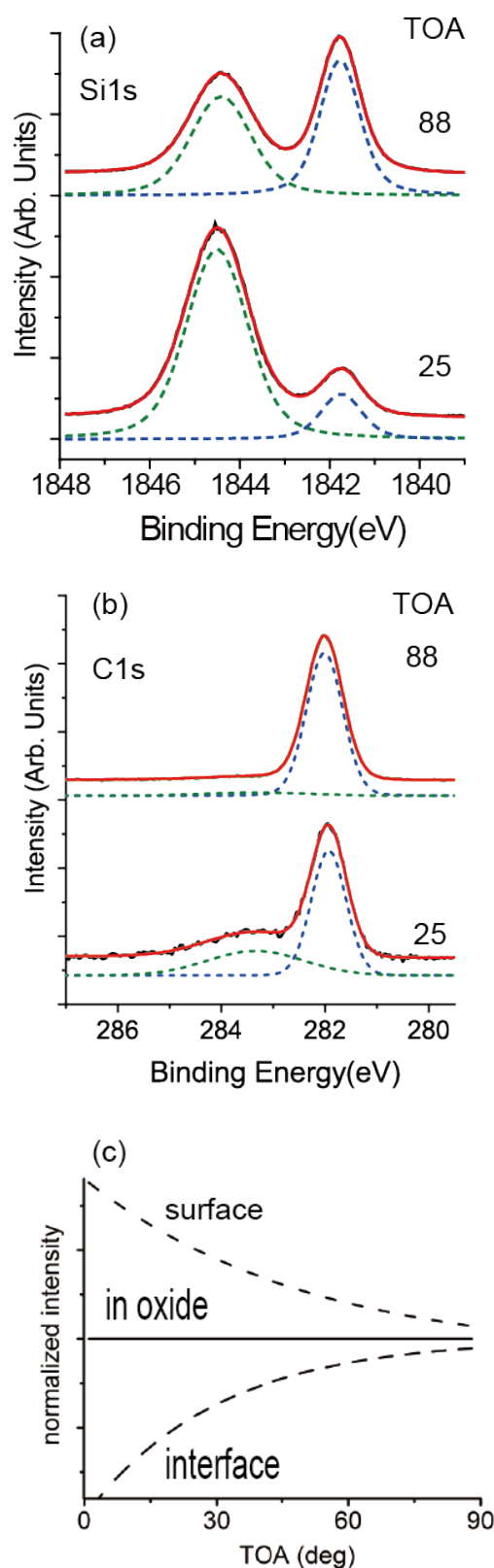


Figure 5: Core level spectra for the SiO₂/4H-SiC(0001) structure. (a) Si 1s spectra and (b) C 1s spectra. (c) Physical model on carbon cluster intensity normalized by the intensity of SiO₂ as a function of the TOA for three extreme cases: carbon clusters localized at the interface, those distributed uniformly in SiO₂, and those localized only at the surface.

interface states have two components: a uniform structure spanning the SiC band-gap and sharp and large interface states near the CBM. The uniform interface states are assigned to the carbon clusters, while the sharp interface states are attributed to the $\text{Si}_2\text{-C=O}$ and/or $\text{Si}_2\text{-C=C-Si}_2$ states at the interface.

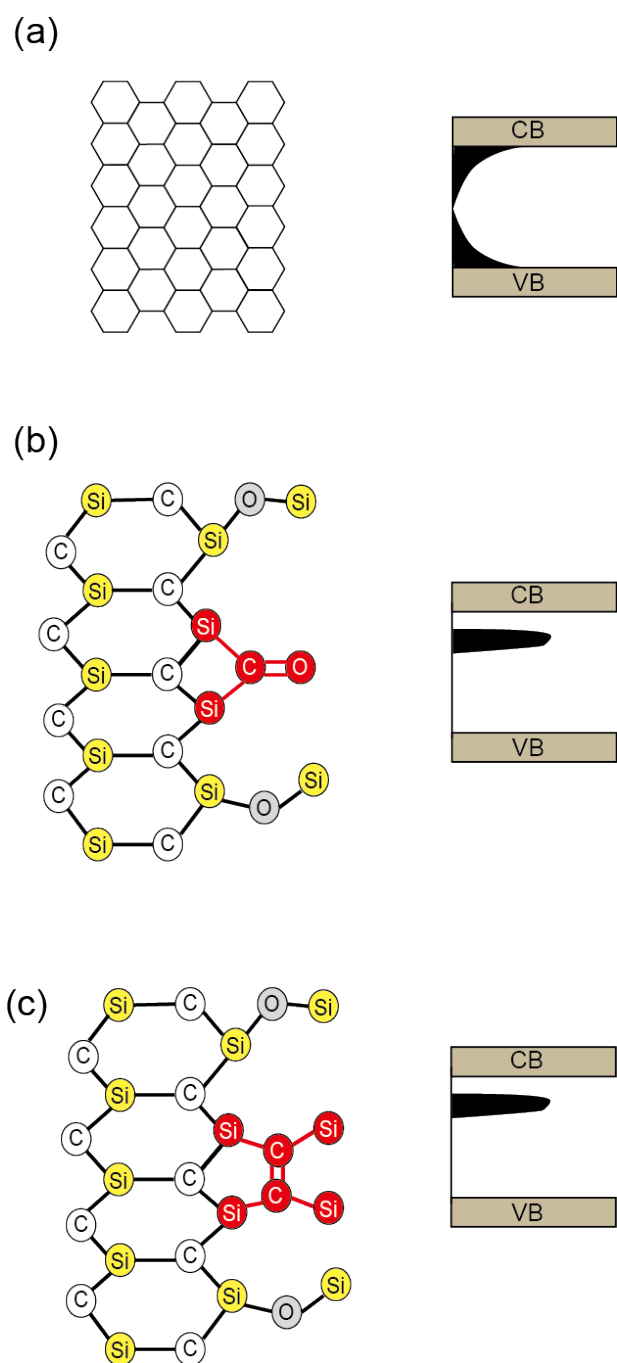


Figure 6: Proposed models of the interface states and the energy level in the band-gap. (a) Carbon cluster, (b) $\text{Si}_2\text{-C=O}$ structure, and (c) $\text{Si}_2\text{-C=C-Si}_2$ structure. SiO_2/SiC interface structures (left) and the corresponding interface state distribution (right).

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