Structures of clean and oxygen-adsorbed SiC(0001)-(3×3) surfaces

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Abstract

The structures of clean and oxygen-adsorbed SiC(0001)-(3×3) surfaces were investigated by high-resolution medium energy ion scattering (MEIS) and photoelectron spectroscopy (PES). The high-resolution MEIS directly evidenced the Si-adatom/trimer/adlayer structure proposed by Starke et al.[Phys Rev. Lett. **80** (1998) 758]. For the surfaces exposed to dry O_2 gas at room temperature, only Si^{4+} and Si^{+} states were observed in the Si 2p core level spectra at an exposure above 10 Langmuir (1 L = 1.0×10^{-6} Torr·sec) and the ratio of Si^{4+} atoms to Si^{+} atoms is almost constant and estimated to be ~1/3. The MEIS analysis demonstrated that the amount of oxygen adsorbed is increased steeply with increasing O_2-exposure up to 10 L and saturated at ~ 50 L with an oxygen coverage of 0.40 ±0.05 ML (1 ML=1.22×10^{15} atoms/cm^2). The above results indicate that the Si-tetramer(adatom/trimer) making the (3×3) periodicity is preferentially oxidized to form a SiO_4-like structure. Such an initial oxidation is intimately related to the reconstructed surface structure and different from those of the SiC(0001)-$\sqrt{3}\times\sqrt{3}$ and Si-rich SiC($000\bar{1}$)-3×3 surfaces, for which all the oxidation states emerge in the former case and Si^{+}, Si^{2+} and Si^{3+} states in the latter.

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1. Introduction

It is well known that silicon carbide surface (SiC) takes various reconstructions depending on the procedure of surface treatments. Typically, annealing temperature and Si-deposition before or during annealing affect the surface structure. In the case of the Si-face denoted by (0001), annealing at 900-950˚C after or during Si-deposition makes a (3×3) reconstruction consisting of Si adatoms. Annealing at higher temperatures of 1000-1050˚C leads to a ($\sqrt{3}\times\sqrt{3}$) structure [1-3] via some metastable phases. The surface changes into a carbon-rich surface with ($6\sqrt{3}\times6\sqrt{3}$) or (6×6) periodicity by annealing at temperatures higher than 1150˚C [4, 5] and the surface is finally graphitized[6].

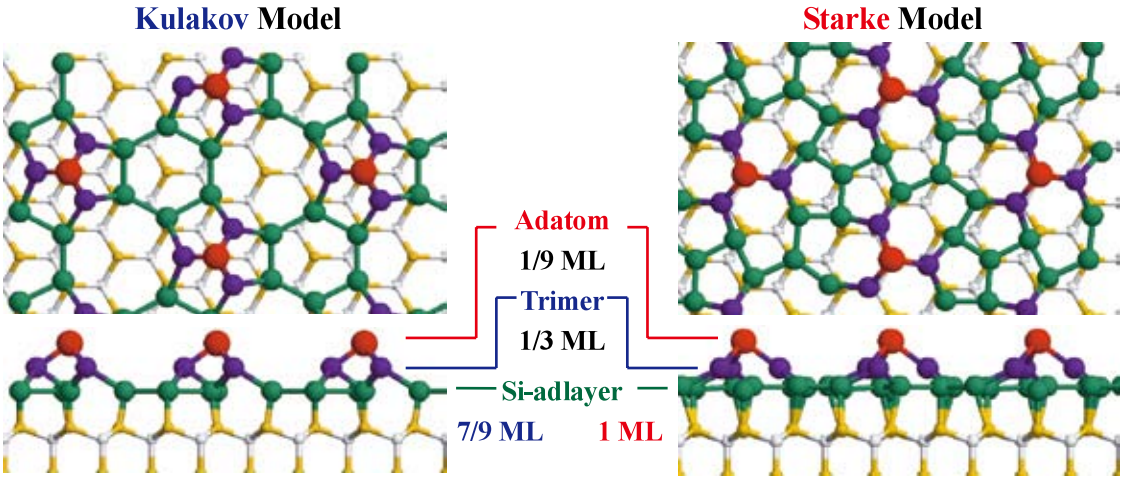

Fig. 1. Surface structures of SiC(0001)-(3×3)-Si proposed by Starke et al. (a) and Kulakov et al. (b). In both models, Si-tetramers (4/9 ML) sit on Si-adlayer, which amounts to 1 ML for Starke model and to 7/9 ML for Kulakov model. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Concerning the 3×3 surface some structure models were proposed so far. Kaplan[7] observed low energy electron diffraction (LEED) patterns and electron energy loss spectra (EELS) and suggested a dimmer- adatoms-stacking-fault (DAS) model known as that for the Si(111)-7×7 surface. A significantly modified structure model was proposed by Kulakov et al.[8] that the 3×3 unit cell consists of eleven Si atoms and their bonding produces three dimers in the first layer and three rest atoms in the second layer making a trimer bonded to an

adatom on top (see Fig. 1(a)). After that Starke et al.[9] proposed a new structure model that a Si tetramer sits on a twisted Si-adlayer with cloverlike rings, as schematically shown in Fig. 1(b). Their analysis using LEED holography combined with scanning tunneling microscopy (STM) ruled out the Kulakov model as well as a simple pyramidal structure model proposed by Li and Tsong[4]. Recently, based on the density-functional theory (DFT) Li et al.[10] showed that besides the Starke model another structure model with fluctuant Si-trimers (FT) and missing Si-adatomas can also reproduce the Patterson maps derived from X-ray diffraction and observed STM image.

There are many reports on oxidation of SiC surfaces from a view point of device fabrications[11-13] and thus the studies concentrate on high-temperature oxidation under high O_2-pressure. Major concern is how to reduce the defect concentrations at oxide/SiC interfaces[14-16]. From a fundamental aspect of surface chemistry, however, the study of the initial oxidation at room temperature (RT) gives some insight into oxidation kinetics correlated to the surface structures and some hint to make an abrupt interface.

In the previous study[17], we observed four oxidation states, Si^{+}, Si^{2+}, Si^{3+} and Si^{4+} for 6H-SiC(0001)-$\sqrt{3}\times\sqrt{3}$ surface oxidized at RT. Contrary to our results, Johansson et al.[18,19] claimed that only two oxidation states, Si^{+} and Si^{4+} appear for the 4H-SiC(0001)-$\sqrt{3}\times\sqrt{3}$ surface oxidized at liquid nitrogen temperature, RT and 800ºC. On the other hand, Amy et al.[20,21] reported that all the oxidation states (Si^{+}, Si^{2+}, Si^{3+} and Si^{4+}) were observed for the 4H-SiC(0001)-3×3 surface oxidized at 25ºC. However, Xie et al.[22] and Chen et al.[23] performed dynamic RHEED rocking analysis combined with *ab initio* calculations and proposed that an O_2 molecule is dissociatively adsorbed on the topmost Si-adatom to form the SiO_2 species at the first step, and then the SiO_4 group is formed by further adsorption of a second oxygen molecule. Quite recently, Voegeli et al.[24] analyzed the structure of the SiC(0001)-(3×3) surface oxidized at O_2-exposure of 200 and 10,000 L using surface X-ray diffraction and their result supported formation of the SiO_4 structure predicted by Xie et al.[22]. As mentioned above, the configurations of oxygen atoms adsorbed on SiC(0001)- (3×3) surface at RT is still a debatable issue.

In the present study, we analyze *in situ* the structures of clean and oxygen-adsorbed SiC(0001)-(3×3) surfaces. The elemental depth profiles are analyzed by high-resolution

medium energy ion scattering (MEIS) in a layer-by-layer fashion. The chemical bonding information is complementally obtained by photoelectron spectroscopy using synchrotron-radiation-light (SR-PES). Our concern is to check the models proposed by Starke et al.[9] and by others[8,10] and to identify the oxygen adsorption sites in initial oxidation for the SiC(0001)-(3×3) reconstructed surface at RT. It is also interesting to compare the oxidation kinetics with those for different surface structures such as SiC(0001)-$\sqrt{3}\times\sqrt{3}$ and Si-rich SiC($000\bar{1}$)-(3×3).

2. Experiment

The present experiments were performed *in situ* at beam line 8 named SORIS at Ritsumeikan SR Center [25]. The SORIS combines high-resolution MEIS and SR-PES under UHV conditions ($\leq 2\times10^{-10}$ Torr). In the MEIS measurements, we used H^+ and He^+ ions accelerated to 120 keV. Well collimated ions were incident along the axes of $[04\bar{4}1]$ and $[08\bar{8}1]$ making angles of 54.7° and 70.5°, respectively, with respect to surface normal in the $(11\bar{2}0)$ plane. Backscattered-ion energies were measured by a toroidal electrostatic analyzer (ESA) combined with three-stage micro-channel plates (MCP) mounted on a position sensitive detector (PSD), which gives an excellent energy resolution ($\Delta E/E$) of 9×10^{-4}. Elemental depth profiles were determined by best-fitting the simulated MEIS spectrum to the observed one assuming an appropriate layered structure. In the spectrum simulation, we employed the Ziegler's stopping powers [26] and the Lindhard-Scharff formula [27] as energy straggling values. For reliable and quantitative analysis, it is indispensable to have the information on the He^+ fractions in equilibrium and non-equilibrium charge states distributions, which are dependent on the emerging velocity, surface materials and emerging angle. It must be noted that the He^+ ions were detected in the MEIS analysis. In order to obtain the reliable data of the absolute amounts of oxygen, we also measured the MEIS spectra using H^+ ions, because the H^+ fraction is independent of emerging angle and scattering depth [28]. Another important factor for precise MEIS analysis is an asymmetric nature of the spectrum, in particular for the scattering component from a top-layer, which comes from the excitation of inner shell electrons during a large angle collision [29]. We approximated a spectrum from each atomic layer as an exponentially modified Gaussian

proposed by Grande et al.[30].

The electron storage ring named AURORA provided intense and linearly polarized photons, which were monochromated with two kinds of gratings in the energy ranges from 10 to 150 eV and from 100 to 500 eV. The energies of emitted photoelectrons were analyzed by a hemispherical ESA with a mean curvature of 137.9 mm. The total energy resolution was estimated to be about 0.1 eV at a pass energy of 2.95eV. Observed spectra were normalized by an integrated beam current of electrons orbiting in the storage ring.

In the present experiment, we used on-axis N-doped 6H-SiC(0001) substrates purchased from CREE Inc. The as-supplied substrates were treated by chemical and mechanical polishing to eliminate some scratches on the surface. After modified RCA cleaning [31], we introduced the sample cut in a typical size of 10×10 mm^2 into an UHV chamber and degassed it at 600 ºC for 5 h by an infrared radiation heater. The Si-rich (3×3) surface of the SiC(0001) face was prepared by annealing at 930 ˚C for 5 min after Si-deposition of ~7 ML and at 1030 ˚C for 5 min. Reflection high energy electron diffraction (RHEED) showed a sharp (3×3) pattern with clear Kikuchi lines and we confirmed no surface contaminations by MEIS and valence band photo-emission spectra.

3. Results and discussion

3.1. SiC(0001)-3×3 surface

Figure 2 shows the MEIS spectra observed for 120 keV He^+ ions incident along the $[04\bar{4}\bar{1}]$-axis and scattered to 85˚, 86˚ and 87˚ scaled from the surface normal. The larger the emerging angle, the better the depth resolution. The arrow $E_{Si}^{(1)}$ corresponds to the energy position for the scattering component from the Si atoms in the first Si-C bilayer. This is judged from the peak position for the scattering component from the C atoms in the first bilayer which is shifted toward the lower energy side (not shown here). The peaks on the higher energy side are identified as the components from adsorbed Si layers on the first bilayer. The total amount of Si on the first Si-C bilayer is derived to be ~1.5 ML, which is consistent with the value of 1.44 (13/9) ML expected from the Starke model but considerably larger than that from the Kulakov (11/9 ML) and DAS (10/9 ML) models. As clearly seen, the observed three MEIS spectra are well reproduced by assuming the Starke model (solid

curves). Note that if an elemental depth profile is given, the corresponding MEIS spectrum is easily constructed[32]. The three components with peak positions located at $E_{Si}^{(a)}$, $E_{Si}^{(b)}$ and $E_{Si}^{(c)}$ come from the Si adatoms (1/9 ML), trimers (3/9 ML) and adlayer (1 ML), respectively.

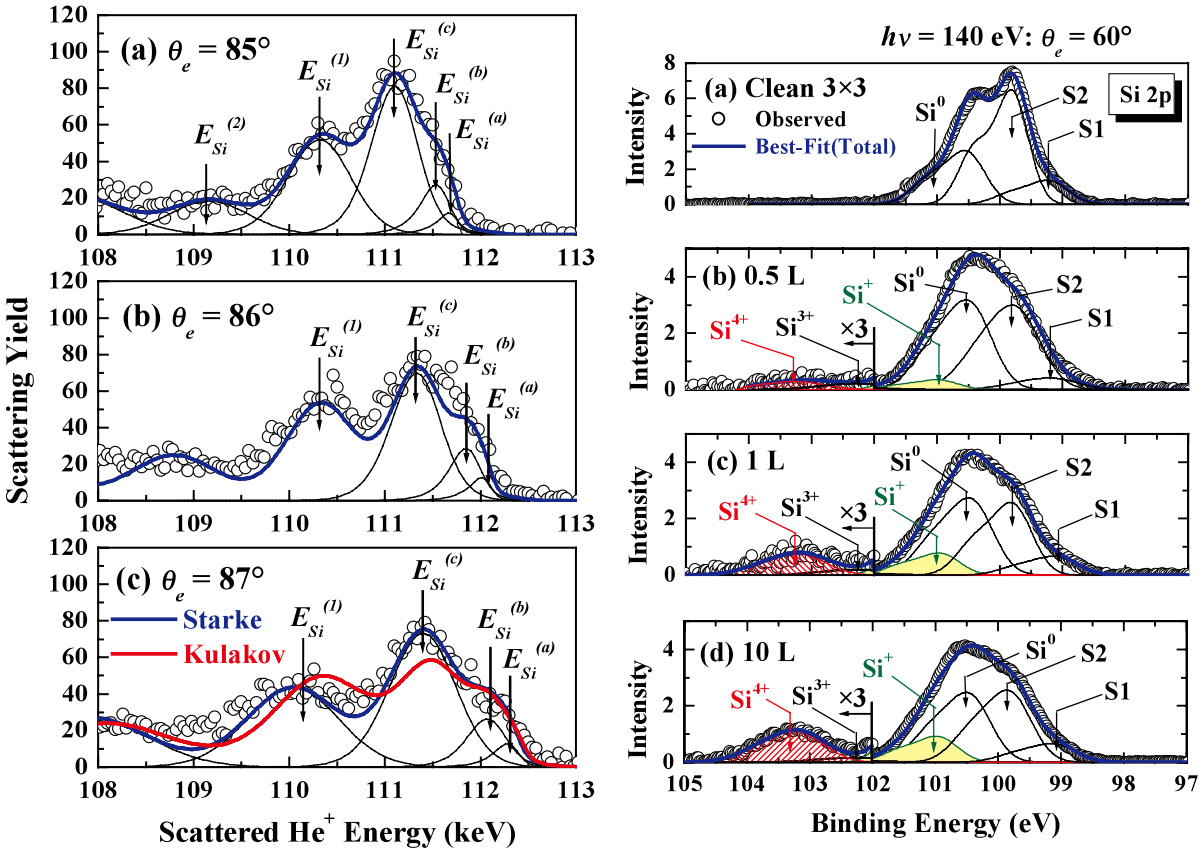

Fig. 2. MEIS spectra observed at different emerging angles scaled from surface normal. The arrow $E_{Si}^{(1)}$ corresponds to the energy position for the scattering component from the Si atoms in the first Si-C bilayer. The arrows denoted by $E_{Si}^{(a)}$, $E_{Si}^{(b)}$, and $E_{Si}^{(c)}$ indicate the components from adatom-Si, trimer-Si, and adlayer-Si, respectively. The solid curves are simulated spectra assuming Starke model. The red curve drawn in the bottom (c) is simulated one assuming Kulakov model

Fig. 3. Si 2p core level spectra observed for (a) clean and oxidized ((b) 0.5L, (c) 1L, (d) 10L) samples at photon energy of 140eV and exit angle of 60˚ with respect to surface normal.

The red solid curve drawn in Fig. 2 (c) is the simulated MEIS spectrum assuming the Kulakov model (Si adatoms: 1/9 ML, trimers: 3/9 ML, adlayer: 7/9 ML). Apparently, the present MEIS analysis rules out the Kulakov model and confirms the validity of the Starke model

rather than the model with fluctuant Si-trimers and missing Si-adatoms[10].

We measured Si 2*p* core level spectra with SR-photon of 140 eV at an exit angle of 60° with respect to surface normal, which are shown in Fig. 3. The spectrum (Fig. 3(a)) contains two surface-shifted components (S1: 98.86±0.1 eV and S2: 99.54±0.1 eV) other than that of the bulk (Si^0: 100.24±0.1 eV), which are consistent with the data reported by Amy et al.[33]. Considering the intensity ratio of S1/S2 dependent on photon energy and emission angle, the surface-shifted components S1 and S2 originate from the Si-adatoms and from the Si-trimers plus Si-adlayer, respectively in the Starke's model. Recently, Virojanadara and Johansson[34] observed three surface-shifted components (SS1: –1.5 eV, SS2: –1.0 eV, SS3: –0.6 eV scaled from bulk component) by high-resolution PES and suggested them to correspond to Si adatoms, Si-trimer plus Si adlayer and Si atoms in the first S-C bilayer, respectively. The above SS1 and SS2 correspond to S1 and S2, respectively and the SS3 component was not resolved in the present PES analysis. Aside from the above assignments, *ab initio* electronic structure calculations[35] predicted also three components of exchange splittings into the Si adatom 2p core levels. Unfortunately, the above splitting is not detected due to the constraint of energy resolution and overlapping of the other surface-shifted components.

3.2. Oxidation of SiC(0001)-3×3 surface at RT

The (3×3) surface was then exposed to oxygen molecules up to several hundreds Langmuir (1 L = 1.0×10^{-6} Torr·sec) at RT. The (3×3) RHEED pattern was clearly observed for the samples exposed to O_2 up to 5,000 L. The absolute amount of oxygen adsorbed was measured *in situ* by MEIS and shown in Fig. 4. It is found that the O-coverage is increased abruptly up to 10 L (0.35±0.05 ML) and then saturated with 0.40±0.05 ML at O_2-exposure of ~ 50 L. The coverage of oxygen is comparable with the number of Si atoms composing the Si-tetramer (adatom + trimer: 4/9 ML), suggesting the Si-tetramer as an adsorption site.

Figure 3(b)-(d) shows the Si 2p core level spectra observed for the samples oxidized at O_2-exposures of 0.5, 1.0, and 10 L. For a small O_2-exposure below 0.5 L, the Si^+ species is seen as a primary oxidation state and simultaneously the intensity of the surface-shifted component S1 is abruptly decreased. Here, as the binding energy (E_B) of the Si^+ state, we

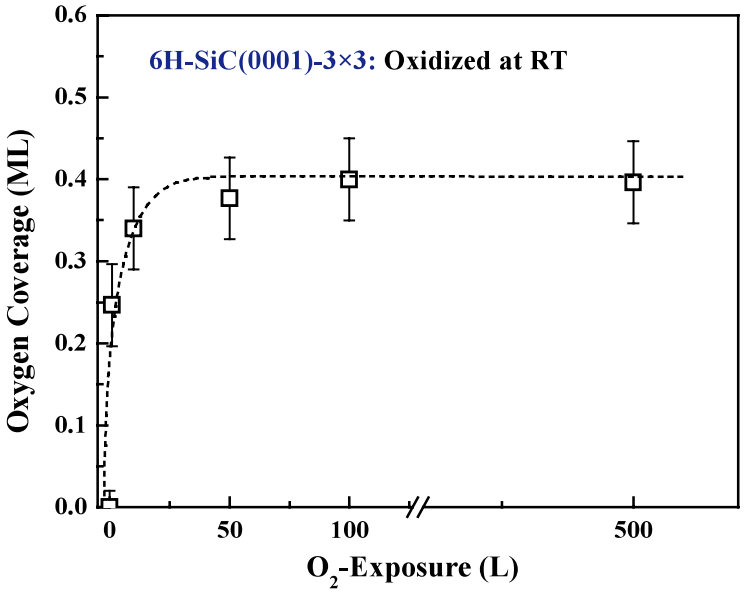

Fig. 4. Absolute amounts of adsorbed oxygen estimated from MEIS as a function of O_2-exposure (L).

adopt the value of +0.5 eV relative to the bulk component for oxidized SiC(0001), which was reported by Glans et al. [36] and Virojanadara and Johansson [37]. The surface state band originating from the dangling bond of Si-adatoms seen in the band gap for the clean (3×3) surface[38] also becomes invisible (not shown here). This indicates that oxygen molecules are first adsorbed to the dangling bond of Si-adatoms and thus rules out the oxygen incorporation into the lower Si layer far away from the tetramer which was suggested by Amy et al.[20]. The Si^{4+} state appears at an O_2-exposure above 0.5 L and the spectrum shape does not change significantly by further O_2-exposure up to 10 L, although the intensities of Si^{+} and Si^{4+} states increase gently up to 50 L. This is consistent with the previous MEIS result. Apparently, the primary oxidation states are Si^{+} and Si^{4+} species and the contribution from Si^{2+} and Si^{3+} states are negligibly small above oxygen exposure above 1 L (the E_B shifts of Si^{2+} and Si^{3+} are derived by trisecting the interval of E_B between the Si^{+} and Si^{4+} states). Figure 5 shows the relative intensities of S1, Si^{+}, Si^{4+} and the ratio of Si^{+}/Si^{4+} measured at photon energy of 140 eV as a function of oxygen exposure. The ratio of relative abundance of Si^{4+}/Si^{+} is derived to be ~1/3 for O_2-exposure above 50 L. Here, the ratio of photo-ionization cross section for $\sigma_{Si^{4+}} / \sigma_{Si^{+}}$ is assumed to be 2.4, which was previously measured for the Si(111)-7×7 surface

oxidized at RT[39].

Now, we propose a probable atomic configuration of the SiC(0001)-3×3 surface oxidized at RT. Amy et al.[20,21] reported that all the oxidation states (Si^{+}, Si^{2+}, Si^{3+} and Si^{4+}) appeared for the 4H-SiC(0001)-3×3 surface oxidized at 25ºC. They assigned the component with an E_B shift of +2.48 eV to the Si^{3+} state, probably inferred from the oxidation states of Si(111)[40] (see Table I). This component should be regarded as the Si^{4+} state of the $SiO_4(Si^{4+})$ group. It is not clear at the present that the E_B shift of Si^{4+} determined here is considerably larger than that reported by Virojanadara and Johansson[34]. They used 4H-SiC(0001) substrates and performed thermal oxidation at 800ºC. Our PES and MEIS analyses clearly show the SiO_4 structure (ad-ins×3) formed at O_2-exposure more than 10 L, as observed in oxidation of the Si(111)-7×7 surface[39] at RT. Here, "ad" means an O atom bonded on top of the Si adatom and "ins-*n*" denotes *n* O atoms singly inserted into *n* Si adatom back-bonds. This (ad-ins×3) structure remains stably up to O_2-exposure of 500 L at RT, because the Si^{4+}/Si^{+} ratio takes a constant value of ~1/3 and the saturated O-coverage of 0.40±0.05 ML determined by MEIS is compatible with 4/9 ML which is expected if the SiO_4 structure is completely formed. It must be noted again that the (3×3) RHEED pattern was clearly seen for O_2-exposure up to 5,000L. The present conclusion is quite consistent with the prediction of Xie et al.[22] and Chen et al.[23] based on dynamic RHEED rocking analysis combined with *ab intio* calculations and also with the surface-X-ray diffraction analysis by Voegeli et al.[24]

It is noteworthy that such an initial oxidation at RT is different from those of the SiC(0001)-$\sqrt{3}\times\sqrt{3}$ and SiC($000\bar{1}$)-(3×3) surfaces, because drastic change of surface atomic configurations is significantly suppressed at low temperature oxidation. It is widely accepted that the $\sqrt{3}\times\sqrt{3}$ surface consists of Si-adatoms of 1/3 ML located at T4 site on the Si-C bilayer[43]. Concerning the SiC($000\bar{1}$)-(3×3) surface, Hoster et al.[44] proposed a structure like the Kulakov model with missing Si-adatoms based on their observation of scanning tunneling microscopy. However, *ab initio* first principles calculations predicts that such structures of Si-trimer/adlayer with and without Si-adatoms are unstable on the C-face[45].

Shown in Table 1 are the binding energy (E_B) shifts of the oxidation states relative to the bulk

E_B value in comparison with the data reported so far. In the previous study[17], we observed four oxidation states, Si^{+}(60 %), Si^{2+}(18 %), Si^{3+}(5 %) and Si^{4+}(17 %) and an O-coverage of 1.07±0.05 ML saturated at 10 L for 6H-SiC(0001)-$\sqrt{3}\times\sqrt{3}$ surface oxidized at RT. Here, we must note that if oxygen atoms are inserted into the on-top and three back bonds of Si-adatoms, the Si^{4+}/Si^{+} ratio and saturated O-coverage should be 1/3 and 1.33 ML, respectively. Therefore, the configuration of oxygen adsorbed on the $\sqrt{3}\times\sqrt{3}$ surface is different from that on the (3×3) surface. Concerning the SiC($000\bar{1}$)-(3×3) surface, we found that the Si^{+}, Si^{2+} and Si^{3+} states emerged and the O coverage was saturated with 0.35 ML at ~5 L. This suggests that there exist no Si-tetramers like that for SiC(0001)-3×3 surface, as predicted by the *ab initio* calculations[45] mentioned before.

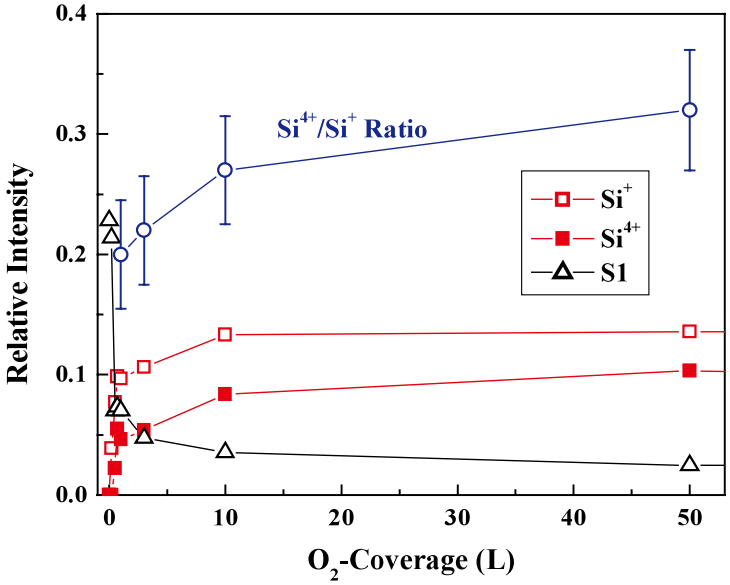

Fig. 5. Relative intensities of S1, Si^{+} and Si^{4+} states together with the ratio of relative abundance Si^{4+}/Si^{+} as a function of O_2-exposure. The ratios of Si^{4+}/Si^{+} abundance are corrected assuming the ratio of photo-ionization cross sections ($\sigma_{Si^{4+}}/\sigma_{Si^{+}}$) of 2.4.

model and evidences the Starke model rather than the model with fluctuant Si-trimers and missing Si-adatoms. We oxidized the clean (3×3) surface at O_2-exposure of 0.2 – 1000 L at RT. Oxidation is almost saturated at ~50 L and the saturated oxygen coverage is estimated to be 0.40±0.05 ML. At low O_2-exposure below 0.5 L, the Si^{+} state is seen dominantly in the Si 2p core level spectra and the surface state band originating from dangling bonds disappears in the valence band spectra. At higher O_2-exposure, the Si^{+} and Si^{4+} oxidation states were

primarily observed and the ratio of relative abundance Si^{4+}/Si^{+} is derived to be ~1/3 at O_2-exposure more than 10 L. The saturated oxygen coverage of ~0.4 ML close to the coverage of Si-tetramers (4/9 ML) and the Si^{4+}/Si^{+} ratio of ~1/3 indicate preferential oxidation of Si-tetramers on top and formation of an (ad-ins×3) structure similar to oxidation of the Si(111)-7×7 surface. The present result is quite consistent with the surface X-ray diffraction analysis and the DFT prediction that an O_2-molecule is preferentially adsorbed to a dangling bond site (Si-adatom) dissociatively and via (ins-*n*: *n* = 1, 2 and 3) states an (ad-ins×3) structure is formed finally. It is emphasized that the oxidation at low temperatures is well correlated with the structure of surface reconstructions. Indeed, the primary oxidation states for the SiC(0001)-3×3 surface are quite different from those for SiC(0001)-$\sqrt{3}\times\sqrt{3}$ and Si-rich-SiC($000\bar{1}$)-3×3 surfaces.

Table 1: Binding energy shifts of Si oxidation states from the bulk (Si^0) component (eV)

	face	Si^+	Si^{2+}	Si^{3+}	Si^{4+}
Present	6H-SiC(0001)-3×3	+0.50			+2.75
Takeuchi et al. [38]	6H-SiC($000\bar{1}$)-3×3	+0.50	+1.05	+1.6	
Hoshino et al. [41]	6H-SiC($000\bar{1}$) -2×2			+1.6	+2.75
Hollering et al. [42]	6H-SiC($000\bar{1}$) -2×2			+1.8	
Hoshino et al.[17]	6H-SiC(0001)-$\sqrt{3}\times\sqrt{3}$	+0.50	+1.07	+1.63	+2.2
Glans et al. [36]	6H-SiC(0001)-$\sqrt{3}\times\sqrt{3}$	+0.50			+2.2
Virojanadara and Johansson [37]	4H-SiC(0001)-$\sqrt{3}\times\sqrt{3}$	+0.50			+2.2
	4H-SiC($000\bar{1}$)-3×3		+1.5		+2.7
Virojanadara and Johansson [34]	4H-SiC(0001)-3×3	+0.6			+2.1
Chen et al. [23]	6H-SiC(0001) -3×3			+1.7*	+2.6
Amy et al. [20]	α-SiC(0001) -3×3	+0.25	+1.36	+2.48	
Himpsel et al. [40]	Si(111)-7×7	+0.95	+1.75	+2.48	+3.9

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References

[1] J.E. Northrup, J. Neugebauer, Phys. Rev. B **52** (1995) R17001.

[2] T. Fujino, T. Fuse, J.-T. Ryu, K. Inudzuka, Y. Yamazaki, M. Katayama, K. Oura, Jpn. J. Appl. Phys. **39** (2000) 6410.

[3] A. Coati, M.S. Simkin, Y. Garreau, R. Pinchaux, T. Argunova, K. Aïd, Phys. Rev. B **59** (1999) 12224.

[4] L. Li, I.S.T. Tsong, Surf. Sci. **351** (1996) 141.

[5] F. Owman, P. Mårtensson, Surf. Sci. **369** (1996) 126.

[6] Th. Seyller, K.V. Emtsev, K. Gao, F. Speck, L. Ley, A. Tadich, L. Broekman, J.D. Riley, R.C.G. Leckey, O. Rader, A. Varykhalov, A.M. Shikin, Surf. Sci. **600** (2006) 3906.

[7] R. Kaplan, Surf. Sci. **215** (1989) 111.

[8] M.A. Kulakov, G. Henn, B. Bullemer, Surf. Sci. **346** (1996) 49.

[9] U. Starke, J. Schardt, J. Bernhardt, M. Franke, K. Reuter, H. Wedler, K. Heinz, J. Furthmüller, P.Köchkel, F. Bechstedt, Phys Rev. Lett. **80** (1998) 758.

[10] Y. Li, L. Ye, X. Wang, Surf. Sci. **600** (2006) 298.

[11] H. Yano, T. Hirao, T. Kimoto, H. Matsunami, Jpn. J. Appl. Phys. **39** (2000) 2008.

[12] C. Radtke, I.J.R. Baumvol, B.C. Ferera, Appl. Phys. Lett. **85** (2004) 3402.

[13] I. Vickridge, J. Ganem, Y. Hoshino, I. Trimaille, J. Phys. D: Appl. Phys. **40** (2007) 6254.

[14] K. Fukuda, S. Suzuki, T. Tanaka, K. Arai, Appl. Phys. Lett. **76** (2000) 1585.

[15] K.C. Chang, N.T. Nuhfer, L.C. Porter, Q. Wahab, Appl. Phys. Lett. **77** (2000) 2186.

[16] C. Radtke, H. Enriquez, J.C. Arnault, P. Soukiassian, P. Moras, C. Crotti, P. Perfetti, Appl. Phys. Lett. **87** (2006) 193110.

[17] Y. Hoshino, T. Nishimura, T. Yoneda, K. Ogawa, H. Namba and Y. Kido, Surf. Sci. **505** (2002) 234.

[18] C. Virojanadara and L.I. Johansson, Surf. Sci. **519** (2002) 73.

[19] L.I. Johansson, C. Virojanadara, Th. Eickhoff, W. Drube, Surf. Sci. **529** (2003) 515.

[20] F. Amy, H. Enriquez, P. Soukiannian, P.-F. Storino, Y.J.Chabal, A.J.Mayne, G.Dujardin, Y.K. Hwu, C. Brylinski, Phys. Rev. Lett. **86** (2001) 4342.

[21] F. Amy, P. Soukiassian, Y.K. Hwu, C. Brylinski, Phys. Rev. **B 65** (2002) 165323.

[22] X. Xie, K. P. Loh, N. Yakolev, S.W. Yang, P. Wu, J. Chem. Phys. **119** (2003) 4905.

[23] W. Chen, X.N. Xie, H. Xu, A.T.S. Wee, K.P. Loh, J. Phys. Chem. **B 107** (2003) 11597.

[24] W. Voegeli, K. Akimoto, T. Urata, S. Nakatani, K. Sumitani, T. Takahashi, Y. Hisada, Y. Mitsuoka, S. Mukainakano, H. Sugiyama, X. Zhang, H. Kawata, Surf. Sci. **601** (2007) 1048.

[25] Y. Kido, H. Namba, T. Nishimura, A. Ikeda, Y. Yagishita, Nucl. Instrum. Methods **B 136-138** (1998) 798.

[26] Z.F. Ziegler, J.P. Biersack, and W. Littmark, *The Stopping and Range of Ions in Matter* (Pergamon, New York, 1985).

[27] J. Lindhard and M. Scharff, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd. **27**, No. 15 (1953).

[28] T. Okazawa, T. Nishimura, K. Shibuya, Y. Kido, Nucl. Instrum. Methods Phys. Res. **B 256**, 1 (2007).

[29] P.L. Grande and G. Schiwietz, Phys. Rev. **A 58**, 3796 (1998).

[30] P.L. Grande, A.Hentz, R.P.Pezzi, I.J.R. Baumvol, G.Schiwietz, Nucl. Instrum. Methods **B 256** (2007) 92.

[31] W. Kern, D.A. Poutinen, RCA Rev. **31** (1970) 187.

[32] T. Nishimura, T. Okazawa, Y. Hoshino, Y. Kido, K. Iwamoto, K. Tominaga, T. Nabatame, A. Toriumi, J. Appl. Phys. **96** (2004) 6113.

[33] F. Amy, P. Soukiannian, Y.K. Hwu, C. Brylinski, Surf. Sci. **464** (2000) L691.

[34] C. Virojanadara and L.I.Johansson, Phys. Rev. **B 71** (2005) 195335.

[35] V.I. Anisimov, A.E. Bedin, M.A. Korotin, G. Santoro, S. Scandolo, E. Tosatti, Phys. Rev. **B 61** (2000) 1752.

[36] P.-A. Glans, T. Balasubramanian, M. Syväjärvi, R. Yakimova, L.I. Johansson, Surf. Sci. **470** (2001) 284.

[37] C. Virojanadara and L.I. Johansson, Surf. Sci. **505** (2002) 358.

[38] F. Takeuchi, R. Fukuyama, Y. Hoshino, T. Nishimura, Y. Kido, Surf. Sci. **601** (2007) 2203.

[39] T. Nishimura, Y. Hoshino, H. Namba and Y. Kido, Surf. Sci. **461** (2000) 146.

[40] H.J. Himpsel, F.R. McFeely, A. Taleb-Ibrahimi, J.A. Yarmoff, G. Hollinger, Phys. Rev.

B 38 (1988) 6084.

[41] Y. Hoshino, F. Fukuyama, Y. Kido, Phys. Rev. **B 70** (2004) 165303.

[42] M. Hollering, F. Maier, N. Sieber, M. Stammler, J. Ristein, L. Ley, A.P.J. Stampfl, J.D. Riley, R.C.G. Leckey, F.P. Leisenberger, F.P. Netzer, Surf. Sci. **422** (1999) 531.

[43] J.E. Northrup and J. Neugebauer, Phys. Rev. **B 52** (1995) R17001.

[44] H.E. Hoster, M.A. Kulakov and B. Bullemer, Surf. Sci. **382** (1997) L658.

[45] S. Tanaka, private communication.