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We investigate the β-SiC(100)3×2 surface oxidation by core level and valence band photoemission spectroscopies using synchrotron radiation. Low molecular O_2 exposures on the (3×2) surface reconstruction leads to direct SiO_2/β-SiC(100)3×2 interface formation already at room temperature (RT). To our best knowledge, this is the first example of RT oxidation leading directly to dominant silicon dioxide growth by O_2 chemisorption only. The amount of SiO_2 is enhanced when the surface temperature is raised by few hundred degrees only (<500 °C) during O_2 exposures leading to ''bulk oxide'' formation already at small thicknesses. These findings are also relevant in low-temperature semiconductor oxide processing. © *1996 American Institute of Physics.* [S0003-6951(96)04214-0]

Silicon carbide (SiC) is a promising IV-IV compound semiconductor having a strong technological interest.[1] In fact, this ''refractory'' semiconductor could be very useful in its ability to provide devices able to operate at rather elevated temperatures (≈600 °C), especially when compared to conventional semiconductors as silicon (<150 °C). However, unlike many other elemental or compound semiconductors, SiC has so far received much less attention in surface science. One of the key issues in successful device applications is surface oxidation. Despite its major importance, this was not very much investigated in surface/interface science, with few studies only on direct and promoted oxidation of SiC surfaces.[2–5] These investigations were performed using conventional techniques,[2–5] with, unlike Si surfaces, no such SiC oxidation studies using synchrotron radiation.

In this letter, we present the first investigation of SiC oxidation using synchrotron radiation. We show that ''bulk-like'' SiO_2 could be grown already at small thicknesses on the β-SiC(100)3×2 surface (Si-rich) at low surface temperatures and low O_2 exposures. SiO_2 is found to be the dominant oxide product already at room temperature (RT). To our best knowledge, these findings, which bring very new insights in understanding low-temperature oxide growth and in SiC surface oxidation, have never been observed previously even on Si surfaces. This shows the central importance of surface structure in the successful growth of SiO_2.

The photoemission experiments were performed at the Synchrotron Radiation Center, University of Wisconsin-Madison using the 1 GeV Aladdin storage ring and ''grasshopper'' Mark II or Mark V monochromators. The photoelectron energy was measured by a cylindrical mirror analyzer. The overall energy resolution of ~0.4 eV at Si 2*p* and ≈1.1 eV at C 1*s* core levels was established from a gold film also providing Fermi level position. Single-domain β-SiC(100) thin films (≈1 μm) were prepared at LETI by chemical vapor deposition on a Si(100)2×1 wafer miscut by 4°. Native oxides removal is achieved by annealing at 1150 °C resulting in clean and carbon rich surfaces. Subsequent Si deposition, using a carefully outgassed Si source, followed by thermal annealings at 950 °C for 10 min produce clean single-domain (3×2) surfaces, as checked by sharp low-energy electron diffraction (LEED) patterns. To avoid photochemical effects, the beam line was closed during oxygen exposures. We have decomposed the Si 2*p* spectra using conventional combination of Lorentzian and Gaussian functions to take into account both Si 2*p* life time and instrumental broadening. We used a branching ratio of 0.5, a 0.6 eV spin-orbit splitting and a 0.1 eV Lorentzian width.[6,7] Other experimental details could be found elsewhere.[5,8]

We first look at the clean β-SiC(100)3×2 surface using the Si 2*p* core level (Fig. 1) recorded in both bulk- and surface-sensitive modes (at photon energies $h\nu$ of 115 and 150 eV). The Si 2*p* spectra are decomposed into three components A, B, and C at binding energies of 99.2, 100.2, and 99.5 eV, respectively. The 99.2 eV component (A), located at same binding energy than pure Si, which could result from Si ad-atoms, is also assigned to the presence of Si clusters resulting from Si deposition during the 3×2 surface preparation. In fact, for β-SiC(100)3×2 surfaces prepared with longer Si deposition time, we clearly observe the same three peaks (A, B, C,) by a simple visual inspection.[9] Peak A visually disappears after thermal annealings but could still be identified after peak decomposition (Fig. 1, two bottom spectra), thereby supporting further its assignment to Si clusters. Peak A is also visible on the two top spectra (Fig. 1) after a 10^{+4} Langmuir (1 Langmuir=1 L=10^{-6} Torr-s) oxygen exposure at 300 and 500 °C. Component B is related to Si–C bonds corresponding to bulk SiC and peak C to the top Si surface layer in the (3×2) structure.[6,7]

We now turn to the oxidation study using the Si 2*p* core level (Fig. 1) for an oxygen exposure of 10^{+4} L at temperatures ranging from 25 to 500 °C. In order to make comparison with silicon oxidation easier, the spectra are presented

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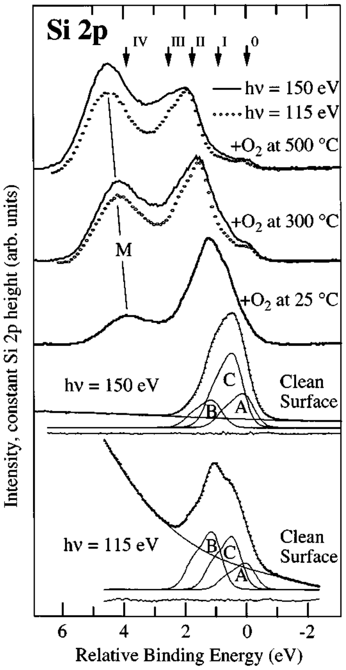

FIG. 1. Si 2*p* core level for clean β-SiC(100)3×2 surface and exposed to 10^{+4} L of O_2 at various temperatures ranging from 25 to 500 °C. The photon energy was 150 and 115 eV for surface and for bulk sensitive modes, respectively. For comparison, bars (0 to IV) indicates various Si oxidation states (Si^0, Si^+, Si^{2+}, Si^{3+}, and Si^{4+}) bonding energies in the case of very thin silicon oxides (see. e.g., Ref. 10). The two bottom spectra show the Si 2*p* core level decompositions, fits, background subtraction, and residual background for the clean β-SiC(100)3×2 surface in bulk- (bottom) and surface-sensitive (second from bottom) modes.

with a relative binding energy scale having its origin at the Si $2p_{3/2}$ component of pure silicon. Upon RT O_2 exposure, the Si 2*p* core level, recorded in the surface sensitive mode ($h\nu = 150$ eV) exhibits a new chemical component (Peak *M*) shifted by 3.9 eV to higher binding energy at 103.1 eV. This indicates the formation, already at room temperature, of silicon oxides having very high oxidation states as SiO_2. It shows that the β-SiC(100)3×2 surface behaves very differently from the silicon ones for which RT O_2 exposures result in lower oxidation states, primarily as Si^{3+}.[10]

We study next the effect of surface temperature on the β-SiC(100)3×2 surface oxidation. When the 10^{+4} L of O_2 exposure is performed at a surface temperature of 300 °C, peak *M* intensity is significantly increased while its energy position is shifted by 4.1 eV at 103.3 eV. This shows that the amount of SiO_2 increases significantly when the surface temperature is raised by few hundred degrees. Also, peak *M* higher binding energy (by 0.2 eV from its previous energy position at RT) indicates that SiO_2 oxide becomes more ''bulk-like''.[11] To get a better insight on the oxide thickness, we recorded the Si 2*p* core level at a photon energy of 115 eV (Fig. 1) which provides a more bulk-sensitive information about the growth of the SiO_2/β-SiC(100)3×2 interface. As can be seen, peak *M* remains intense at lower photoelectron kinetic energies. A surface temperature of 500 °C during O_2 exposure leads to further growth of SiO_2 as evident from peak *M* additional intensity increase with an even larger core level shift ($\Delta E_{Si2p} = 4.5$ eV) at 103.7 eV.

We now look at the other Si 2*p* core level spectral features during oxidation (Fig. 1). The behavior of the major peak between 1 and 2 eV is of special interest. It is likely to result from different contributions. Peak C (related to top Si atoms) collapses during oxidation while peak B (≈1 eV) is still present at lower intensity. Also, the formation, at the interface between SiO_2 and β-SiC(100)3×2 surface, of a complex oxide involving both Si and C atoms as SiOC is likely since it would be consistent with the peak observed around 2 eV. A detailed peak decomposition showing the various oxidation states at the interface will be provided elsewhere.[9] Another interesting feature is the presence (at very low intensity) of peak A at 99.2 eV which could be seen by simple visual inspection for the surfaces oxidized at 300 and 500 °C. It indicates the presence of pure Si clusters which have not been oxidized under the present conditions.

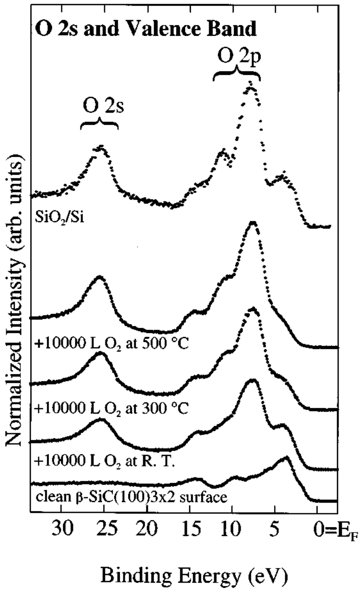

FIG. 2. Valence band and O 2*s* core level for β-SiC(100)3×2 surfaces exposed to 10^{+4} L of O_2 at various temperatures from 25 to 500 °C. For comparison, the valence band of a SiO_2/Si(111)7×7 interface is also presented. The photon energy was 150 eV.

Further valuable insights about SiO_2/β-SiC(100)3×2 interface formation could be found by looking at the valence band. Figure 2 displays the valence band and the O 2*s* core level of this system following the same oxidation sequence described above. For comparison, we also show in Fig. 2 a similar spectrum for a SiO_2/Si interface. Upon oxygen exposures from 25 to 500 °C, the β-SiC(100)3×2 valence band exhibits the growth of O 2*p* electronic levels at binding energies of 7.6, 10.4, and 14.3 eV, characteristic of SiO_2 formation.[10] In fact, as can be seen from the SiO_2/Si valence band, the O 2*p* spectral features are the same. In addition, one can notice that the O 2*s* core level binding energy (25.5 eV) and shape for the SiO_2/β-SiC(100)3×2 and SiO_2/Si(111)7×7 interfaces are identical which further stresses that the oxide products are the same in both cases. Interestingly, the O 2*s* core level does not apparently exhibit a second component.

Additional insights about the atomic bonding configuration could be obtained by looking in Fig. 3 at the C 1*s* core level for the clean and 10^4 L of O_2 exposed β-SiC(100)3×2

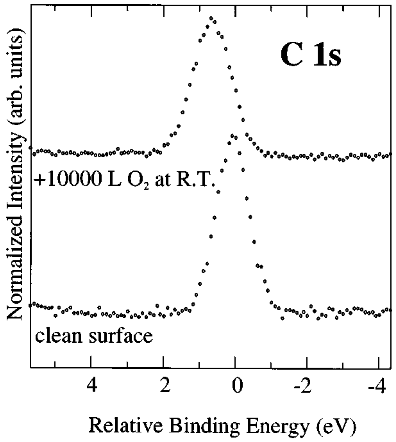

FIG. 3. C 1*s* core level for clean and exposed to 10^{+4} L of O_2 β-SiC(100)3×2 surfaces at room temperature. The photon energy was 340 eV.

surfaces. The C 1*s* core level has been recorded in surface sensitive mode at a photon energy of 340 eV. As can be seen in Fig. 3, the C 1*s* core level is shifted by 0.6 eV to higher binding energy upon exposure with a slight broadening only, suggesting that the C atoms are somewhat involved in the oxidation process. This cannot be related to graphite formation which would result in core level shifts larger than 2 eV.[5,8] Also, it does not seem to indicate presence of direct C–O bonds on the surface, in agreement with the picture obtained from the O 2*s* core level showing only a single component as for SiO_2/Si interface (Fig. 2). In fact, in this case, much larger core level shifts would be expected.[12] However, it is consistent with the formation of a complex oxide as SiOC as suggested above from the Si 2*p* results.

Our above results support the picture of direct SiO_2/β-SiC(100)3×2 interface formation already at RT which, to our best knowledge, is the first observation of this kind. Even on Si surfaces, direct dominant SiO_2 formation could be achieved at much higher temperatures only (above 900 °C). Interestingly, we do not observe a similar behavior with other β-SiC(100) surface reconstructions like (2×1) and (1×1) which are much more difficult to oxidize than Si.[9] This stresses the crucial importance of surface structure in the oxidation process. In fact, the β-SiC(100)3×2 surface is a much more open surface (when compared, e.g., to Si(100)2×1 or to Si(111)7×7) which would allow O atoms to interact more easily with the Si atoms. Furthermore, recent theoretical calculations for Si-rich β-SiC(100) surfaces predicted very large Si–Si dimer bond lengths ($\approx$2.55 Å)[13] indicating weaken Si–Si bonds, especially when compared to the Si(100)2×1 surface having a Si–Si dimer bond length at 2.20 Å.[14] This likely explains the much higher surface reactivity to oxygen of the (3×2) surface reconstruction when compared to silicon surfaces.

The surface reactivity is significantly enhanced when the β-SiC(100)3×2 surface temperature is raised by few hundred degrees (up to 500 °C) during O_2 exposure leading to much larger amounts of SiO_2. Even at 500 °C, the surface temperature remains much lower than temperatures commonly used to achieve SiO_2/Si interface formation. In addition, the SiO_2 oxide layer is carbon free as previously suggested for other SiC surfaces.[2–5] Any direct C oxidation would result in the formation of CO or CO_2 which will desorb from the surface into the vacuum as evident from the lack of any related spectral feature.[2–5] The changes observed at the C 1*s* and Si 2*p* core levels would be more consistent with the presence of a carbon interlayer bonded to SiO_2 and located at the SiO_2/SiC interface. Most significantly, the oxide formed at 500 °C ($\Delta E_{\mathrm{Si}\,2p}=4.5$ eV) corresponds exactly to the binding energy achieved for much thicker oxides (with a 144° Si–O–Si bond angle),[11] despite the fact that here, the oxide thickness is below 10 Å.

In conclusion, we have investigated the direct SiO_2/β-SiC(100)3×2 interface formation by low molecular O_2 exposures using photoemission spectroscopy with synchrotron radiation. Our results indicate that SiO_2($\Delta E_{\mathrm{Si}\,2p}=3.9$ eV) is already the dominant oxidation product at RT. It shows that the nature of surface reconstruction plays a major role in successful oxidation. Raising the surface temperature by only few hundred degrees during O_2 exposure leads to ''bulk-like'' carbon free SiO_2 oxide formation ($\Delta E_{\mathrm{Si}\,2p}=4.5$ eV) already at small thicknesses. These findings bring new and important insights in SiC surface passivation as well as in low temperature oxide formation.

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