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Atomic-layer-resolved bandgap structure of an ultrathin oxynitride-silicon film epitaxially grown on 6*H*-SiC(0001)

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Electronic structures of a silicon-oxynitride (SiON) layer (~0.6 nm in thickness) epitaxially grown on 6*H*-SiC(0001) were investigated on atomic-layer scale using soft x-ray absorption spectroscopy and x-ray emission spectroscopy (XAS and XES) and first-principles calculations. The SiON layer has a hetero-double-layered structure: an interfacial silicon nitride layer and a silicon oxide overlayer. The element-specific XAS and XES measurements revealed layer-resolved energy-band profiles. Measured gap sizes are 6.3 ± 0.6 eV at the nitride layer and 8.3 ± 0.8 eV at the oxide layer. The nitride and oxide layers have almost the same energy of conduction-band minimum (CBM) being ~3 eV higher than CBM of the SiC substrate. The energy-band profiles of the SiON layer are qualitatively reproduced by the calculations. The calculations show that broadening of bandgap of the substrate occurs only at an interfacial SiC bilayer.

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Silicon carbide (SiC) is regarded as a promising material for next-generation power electronic devices because of its wide bandgap, high thermal conductivity, and high electric breakdown field.[1] When a semiconductor material is newly applied to electronic devices, it often meets a problem of how to create a high-quality dielectric/semiconductor interface. SiC-based metal-oxide-semiconductor field-effect-transistor (MOSFET) devices are just facing this problem. Standard oxidation procedures lead to rough SiO_2/SiC interfaces with high defect density, resulting in poor carrier mobility.[2–5]

Recently, we have found that hydrogen-gas etching of a 6*H*-SiC(0001) surface and subsequent annealing in nitrogen atmosphere lead to formation of a crystalline silicon-oxynitride (SiON) layer which exhibits a $(\sqrt{3} \times \sqrt{3})R30°$ periodicity with respect to the ideal SiC(0001) surface. Its atomic structure has been determined by a low-energy electron diffraction analysis.[6] The determined structure is illustrated in Fig. 1. Within the unit cell the interface is atomically abrupt and free from dangling bonds. First-principles calculations have confirmed the structure model and shown that the fundamental bandgap is free from any interface states within the length scale defined by the calculations.[7,8] Due to such interface properties, use of the SiON/SiC(0001) as a seed interface for SiC-MOS structures has been suggested.[6]

In this Rapid Communication, electronic structures of the SiON/SiC(0001) were investigated on atomic-layer scale. As seen in Fig. 1, the SiON layer has a hetero-double-layered structure: an interfacial silicon nitride layer and a silicon oxide overlayer (hereafter denoted as SiN layer and SiO layer for simplicity). Soft x-ray absorption spectroscopy and x-ray emission spectroscopy (XAS and XES) are powerful tools to investigate element-specific electronic structures of such heterolayered materials. Since XAS and XES probe electronic transitions from a core level to conduction states and from valence states to the core hole, respectively, element-specific conduction- and valence-band partial densities of states (PDOSs) can be obtained.[9,10] On the other hand, first-principles calculations can provide atomic-scale properties of electronic states. Combining the experiments and calculations, we obtained electronic structures of the SiON/SiC(0001) on atomic-layer scale. Obtained energy-band profiles of the SiON layer agree between the experiments and calculations qualitatively.

A SiON layer *ex situ* grown on a nitrogen-doped off-axis

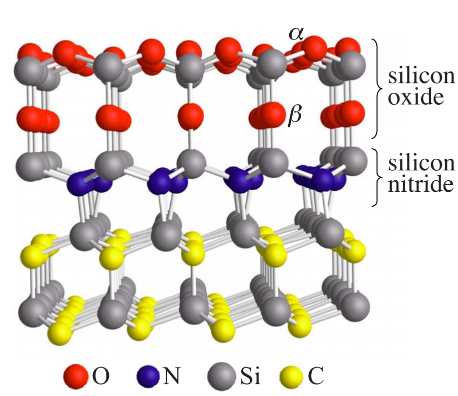

FIG. 1. (Color online) Side view of ball-and-stick model of the SiON/SiC(0001). Two inequivalent O atoms are labeled as α and β.

(4° off toward the [1$\bar{1}$20] direction) 6*H*-SiC(0001) wafer was used as a sample. Sample preparation methods are described elsewhere.[6] Since the sample surface is atomically clean even over a long time in air,[6] any surface cleaning treatment was not carried out prior to measurements.

Experiments were carried out using BL-27SU at SPring-8, Hyogo and BL-12 at SAGA-LS, Saga with linearly polarized synchrotron radiation. O *K*-edge absorption (O $1s \rightarrow 2p$) and N *K*-edge absorption (N $1s \rightarrow 2p$) were measured for XAS spectra at Saga. The absorption spectra were recorded with two methods: measuring sample drain currents as total electron yields (TEYs) and detecting Auger electron yields (AEYs) as element-specific XAS spectra. For AEY measurements, O(*KLL*) and N(*KLL*) Auger electron spectra were recorded using a hemispherical energy analyzer with an energy resolution of 0.4 eV. Energy resolutions of incident photons are 0.2 and 0.1 eV at the O and N *K*-edge absorptions, respectively.

Soft x-ray emissions resulting from electronic transitions of N $2p \rightarrow 1s$ and O $2p \rightarrow 1s$ were measured for XES spectra at Hyogo. Incident angle of excitation photons was at 60° with respect to the surface normal. A flat-field spectrometer consisting of a varied-line-spacing grating and a charge coupled device detector was used. Its design and performance are described in detail elsewhere.[11] Energy resolutions are 0.2 and 0.4 eV for the O- and N-XES spectra, respectively. Photoemission spectroscopy (PES) measurements for O 1*s*, N 1*s*, C 1*s*, and Si 2*p* core levels were carried out with an incident photon energy of 700 eV and an emission angle at 45°. The total energy resolution of the PES measurements was 0.1 eV. The Fermi level (E_F) of the sample was determined by measuring the Fermi edge of an Au film attached to a sample holder.

First-principles calculations were performed with Tokyo *ab initio* program package (TAPP) (Refs. 12 and 13) based on density functional theory (DFT). The exchange-correlation function was Perdew-Burke-Ernzerhof (PBE)96 within the generalized gradient approximation (GGA). A plane-wave basis set was used with a Troullier-Martins-type norm-conserving pseudopotential for Si and ultrasoft pseudopotentials for C, O, N, and H. The surface-Brillouin-zone summation was executed using 49 sample points and the energy cutoff was 36.0 Ry. A calculated system was a supercell model including a SiON layer and eight SiC bilayers where the bottom carbon face is terminated with hydrogen.

Figure 2(a) shows an N 1*s* PES spectrum obtained from the SiON/SiC(0001). The spectrum can be fitted well with a single-component Voigt function as expected from the structure model of Fig. 1 in which there exist single equivalent nitrogen atoms. In Fig. 2(b), N-XAS and N-XES spectra of the SiON/SiC(0001) are plotted as a function of the binding energy (E_B). The origin of the E_B is set to the conduction-band minimum (CBM) of the SiC substrate. Energy location of the CBM was determined from Si 2*p* and C 1*s* core level PES spectra (not shown here). Their peak energies are 0.1 ± 0.1 eV larger than corresponding bulk values reported,[14] indicating a downward surface band bending of 0.1 ± 0.1 eV. Since CBM of *n*-type 6*H*-SiC is located at 0.1 eV above the E_F,[15] the CBM at the substrate surface region

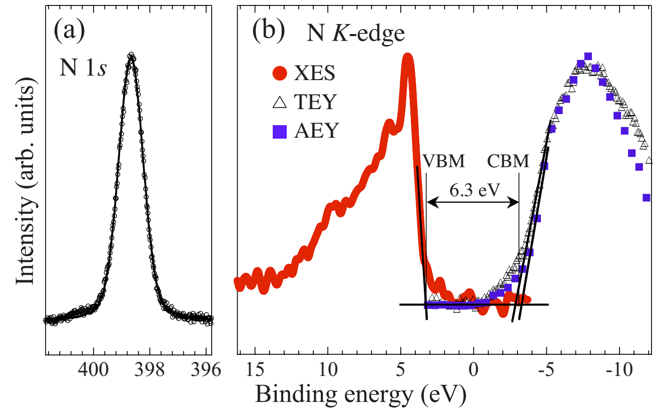

FIG. 2. (Color online) (a) N 1*s* PES and (b) N *K*-edge XES and XAS (TEY and AEY) spectra plotted as a function of the binding energy below CBM of the substrate. Solid line in (a) is the fitted Voigt line. In (b) the XES spectrum was obtained using an excitation energy of 407.2 eV. Solid lines represent extrapolated leading edges of the XAS and XES spectra, which determine the energies of CBM and VBM of the N 2*p* PDOS. Thus obtained bandgap is 6.3 eV.

was coincident with the E_F within the error range. Energy scales of both XAS and XES spectra were converted into the E_B scale via $E_B = (398.7 - h\nu)$ eV, where 398.7 eV is the peak energy of the N 1*s* PES spectrum shown in Fig. 2(a) and $h\nu$ is an energy of adsorbed and emitted photons for XAS and XES spectra, respectively. As seen in Fig. 2(b), the TEY and AEY measurements show essentially the same XAS spectra except for slight disagreement around absorption edges arising from difficulty in a proper background subtraction on the TEY spectra. For N-XES measurement, even though several excitation energies including those over an N 1*s* ionization threshold were employed, the spectral feature did not vary. Therefore, it is concluded that effects of the resonant Raman scattering would be negligible,[16] and thus the spectra reflect the actual PDOS of the N 2*p* valence states. Our calculations confirmed that a sharp peak at $E_B \sim 4.5$ eV in the XES spectrum corresponds to N 2*p* nonbonding state, in agreement with the previous calculation.[8] The N-XAS and N-XES spectra are similar to those obtained from amorphous SiO_xN_y films with ~ 1 nm thickness.[17]

The band edges of the N 2*p* PDOS were determined from intersections between the background level and the extrapolated leading edges of the XES and AEY spectra [see Fig. 2(b)]. The energy of the valence-band maximum (VBM) of the N 2*p* PDOS is estimated to be $E_B = 3.2 \pm 0.2$ eV, where the error arises from uncertainty in the determination of the extrapolated leading edges. The energies of the CBM of the N 2*p* PDOS estimated from the AEY and TEY spectra are -3.3 ± 0.2 and -2.9 ± 0.2 eV, respectively. We thus employ a mean value of -3.1 ± 0.4 eV as the CBM. As a result, the bandgap of the N 2*p* PDOS is estimated to be 6.3 ± 0.6 eV.

Figure 3(a) shows an O 1*s* PES spectrum from the SiON/SiC(0001). The spectrum can be fitted well with a single-component Voigt function, even though the SiON layer contains two inequivalent O atoms having 143 and 180° Si-O-Si bond angles, respectively, denoted as α and β in Fig. 1 (such bond angles can be seen in α-SiO_2- and β-SiO_2 crystals,

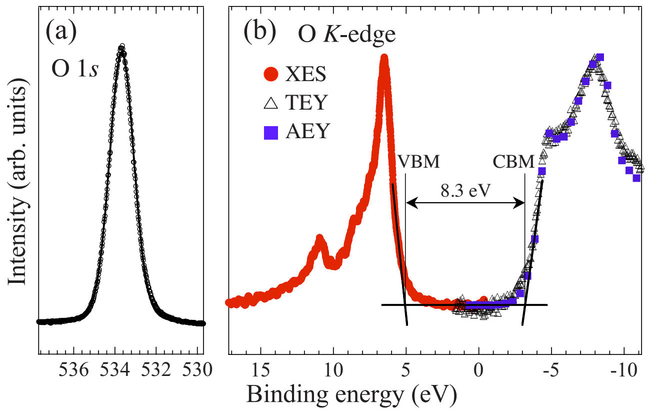

FIG. 3. (Color online) (a) O 1s PES and (b) O K-edge XES and XAS (TEY and AEY) spectra plotted as a function of the binding energy below CBM of the substrate. Solid line in (a) is the fitted Voigt line. In (b) the XES spectrum was obtained using an excitation energy of 541.1 eV. The bandgap of the O 2p PDOS of 8.3 eV is obtained by leading edges of the XAS and XES spectra (solid lines).

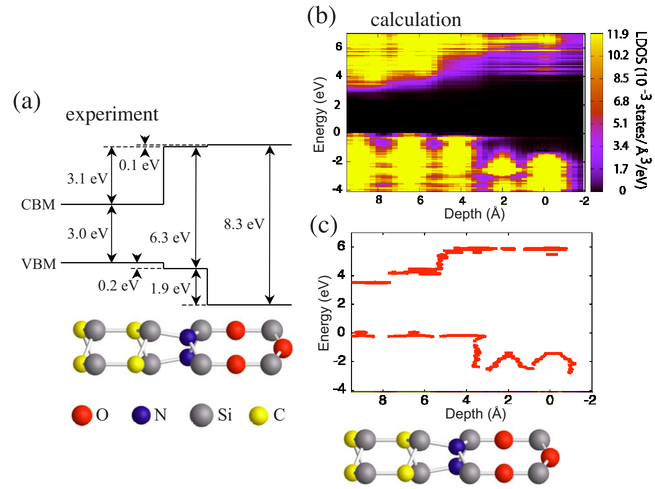

FIG. 4. (Color online) (a) Energy-band profiles of the SiON layer obtained by the XES and XAS measurements. The bandgap of the SiC substrate is assumed to be the bulk value of 3.0 eV. (b) Depth profile of the planar-averaged LDOSs of the SiON/SiC(0001) obtained by the first-principles calculations. The origin of the horizontal axis is the position of the topmost O layer. The topmost Si layer of the SiC substrate is located at the depth of 6.3 Å. The vertical axis is the one-electron energy in eV, whose origin is set to the VBM of the substrate. (c) A threshold LDOS value of 1.0 $\times 10^{-2}$ states/Å^3/eV is plotted at each plane as the band edge. The structure model is illustrated at the bottom of (a) and (c) in accord with the energy-band profiles.

respectively[18]). A possible chemical shift arising from the difference in the bond angle would be small compared with a large lifetime broadening of the O 1s spectrum.

Figure 3(b) shows O K-edge XAS and XES spectra plotted with respect to the E_B. The photon energies were converted into the E_B, via $E_B=(533.7-h\nu)$ eV, where 533.7 eV is the peak energy of the O 1s PES spectrum shown in Fig. 3(a). In Fig. 3(b), the O-XAS spectra obtained by the AEY and TEY measurements agree very well. As mentioned above, there are two inequivalent O atoms in the SiO layer. Since the α- and β-oxygen atoms have distinctly different O-Si bond directions, that is, nearly parallel and exactly perpendicular to the surface plane, their contributions to the TEY spectrum were expected to vary with the incident angle of photon. However, in a range of the incident angle at 0 $\sim 60°$ the spectral shape did not vary. This polarization-independent nature is consistent with nearly isotropic charge-density distributions of CBM states localized at the α- and β-oxygen atoms.[8] Our calculations show that conduction-band PDOSs for the α- and β-oxygen atoms are similar, and their CBMs are almost the same as shown in Figs. 4(b) and 4(c).

The O-XES spectrum in Fig. 3(b) is very similar to those of SiO_xN_y and SiO_2 films.[17] The spectral shape did not vary with excitation energies, indicating that effects of the resonant Raman scattering would also be negligible.[16] Our calculations indicate that a peak at $E_B\sim 6.5$ eV corresponds to O 2p nonbonding states, and a peak at ~ 11 eV to O 2p-Si 3s and 3p hybridization states. These states are also seen in the previous calculations.[8] Energies of the CBM and VBM of the O 2p PDOS are estimated to be -3.2 ± 0.4 and 5.1 ± 0.4 eV in the E_B scale, respectively [see Fig. 3(b)]. The bandgap of the SiO layer is thus 8.3 ± 0.8 eV. This gap size agrees with those obtained by other methods within the error: 8.7 eV measured with scanning tunneling spectroscopy[6] and 8.9 eV from the calculation.[8] These gap sizes are close to that of amorphous SiO_2 of ~ 8.9 eV.[19]

In Fig. 4(a), energy-band profiles obtained from the XAS and XES measurements are summarized to coincide with the structure model. For comparison, a variation in calculated planar-averaged local density of states (LDOS) along the surface normal is depicted in Fig. 4(b). The thickness of each planar layer chosen for averaging is 0.27 Å. Band edges at each plane extracted from Fig. 4(b) are shown in Fig. 4(c) as a guide to the eyes, where a threshold LDOS value of 1.0 $\times 10^{-2}$ states/Å^3/eV is employed as the band edge. This threshold value was determined so that the calculated bandgap at the α-oxygen layer is the same as that of bulk α-SiO_2.[7,8] The calculated energy-band profiles are rather different from those in Ref. 7. This is likely because the LDOSs were obtained by sampling throughout the Brillouin zone in our calculations while only at the Γ point in Ref. 7. Although bandgaps are usually underestimated by DFT/GGA compared with experimental values, the bandgap value at the SiC substrate is slightly larger than the known value of 3 eV. This is due to the quantum confinement effect arising from the slab model as seen in a previous study.[13] Good qualitative agreements can be seen between Figs. 4(a) and 4(c): energy of the CBM is almost constant throughout the SiON layer, and energy of the VBM at the SiN layer is higher than that at the SiO layer.

The bandgap at the interface region of the SiC substrate could not be obtained by XAS and XES measurements because of experimental difficulties.[20] The interfacial bandgap evolution was provided by the calculations. As seen in Figs. 4(b) and 4(c), the bandgap only at the interfacial SiC bilayer (the top layer) is slightly wider than those at deeper layers in the substrate. The atomically abrupt band offset at the SiON/

SiC(0001) interface is undoubtedly superior to typical SiO_2/SiC interfaces, where interface roughness extends as long as a few nm.

Figure 4(c) shows that the bandgap on the SiON layer fully opens at a distance of ~2.5 Å from the topmost layer of the substrate. This result agrees with Ref. 7. This transition length of the bandgap is shorter than ~5 Å which was calculated on an ideal SiO_2/SiC(0001) interface model.[21] A recent comparative theoretical study of various oxide/SiC(0001) interfaces suggests that the presence of the SiN layer assists the rapid evolution of the bandgap at vicinity of the interface.[22] On the SiON layer, the energy locations of the CBM are almost constant, being ~3 eV higher than that on the substrate. This size of the band offset is comparable to that on an ideal SiO_2/SiC interface,[23] which is sufficiently large for reliable operation of the SiC-based MOSFET.[24]

In summary, the atomic-layer-resolved bandgap structures of the SiON/SiC(0001) were revealed by combining the element-specific XAS and XES measurements and the first-principles calculations. The bandgap of the SiON layer was estimated to be 8.3 ± 0.8 eV at the SiO layer and 6.3 ± 0.8 eV at the SiN layer by the XAS and XES measurements. The energy location of CBM on the SiON layer is about 3 eV higher than that on the SiC substrate. The calculations show that widening of the bandgap occurs only at the interfacial SiC bilayer. The ideal band-offset structures suggest use of the SiON/SiC(0001) as a possible seed interface for SiC-MOS structure.

The synchrotron radiation experiments at Hyogo and Saga were performed at BL-27SU in SPring-8 with the approval of JASRI (Proposal No. 2007A2009) and at the BL-12 in the SAGA-LS (Proposal No. 080286N), respectively.

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